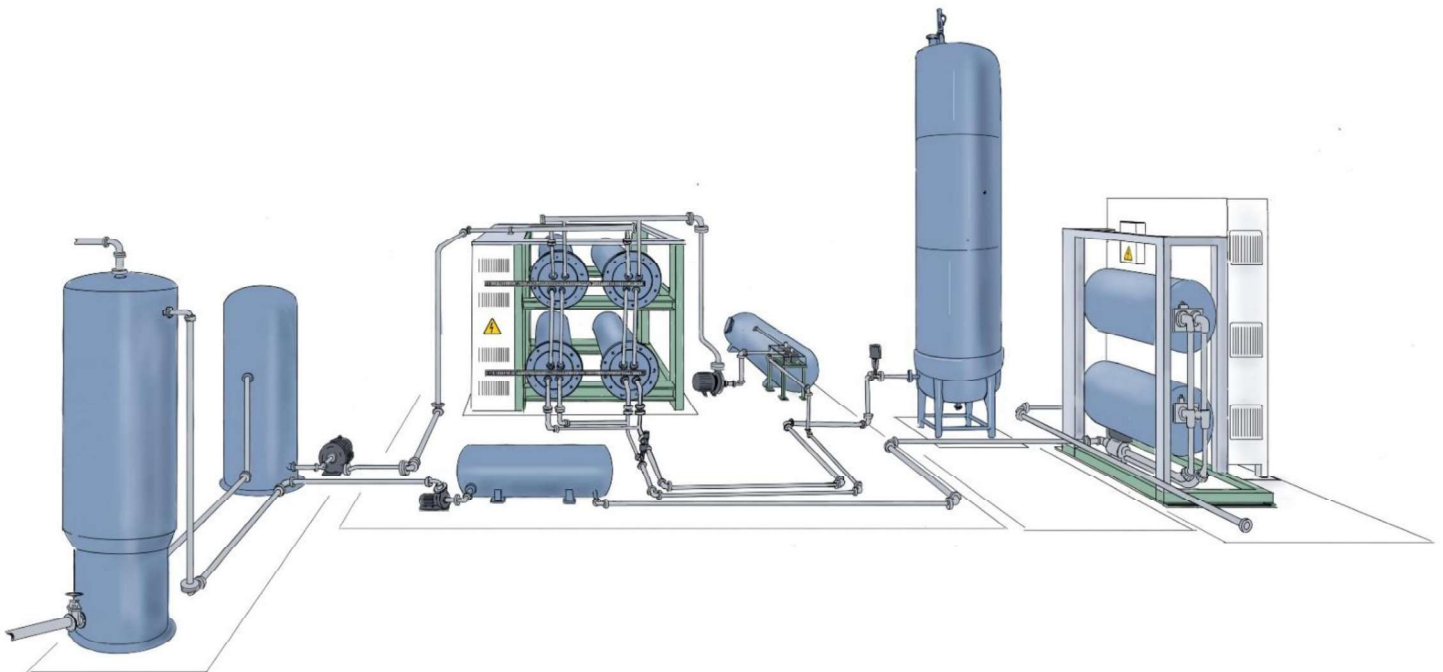


# Power 2 Two Products (P22P)



Delft, 12 February 2020

“Het project is uitgevoerd met subsidie van het Ministerie van Economische Zaken, Nationale regelingen EZ-subsidies, Topsector Energie uitgevoerd door Rijksdienst voor Ondernemend Nederland.”

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## Summary

Coval Energy and TU Delft are involved in a research program to reuse CO<sub>2</sub>, where CO<sub>2</sub> in an electrochemical cell is directly converted to formic acid, a valuable product. Formic acid is one of the most interesting products to make from CO<sub>2</sub>, with the lowest green electricity input per molecule and high current efficiency. As such formic acid is a very interesting candidate for large scale re-use of CO<sub>2</sub>. So far, formic acid is produced at the cathode side of the electrochemical cell. It would be very attractive to also produce a chemical at the anode side of the cell whilst producing formic acid at the cathode, so-called "paired synthesis". The big upside is that the cost of electricity and CAPEX can be divided over both products, which is a potential cost reduction by up to 50%!

This feasibility study has identified chemicals that can be produced in combination with formic acid in an electrochemical cell to achieve this 'paired synthesis'.

The results provide important input for the electrification of the (Dutch) industry. It can help the roll-out of innovative electrification options for the industry, supporting the CO<sub>2</sub> reduction ambitions. It can lead to a higher potential profit for CO<sub>2</sub> capture and utilization, thus increasing the willingness of companies to start capturing their CO<sub>2</sub>, as they do not have to find a solution for storing the CO<sub>2</sub>.

This feasibility project identified the possibility of producing some promising organic chemicals. These chemicals can be electro synthesized at rather low (ambient) temperatures and rather high current densities. The route to propylene oxide can contribute directly to the current aim of electrification of the chemical industry. All major technology needed is commercially available. The route to produce lactobionic acid from lactose has a low current density at present, but it might be a promising candidate after further investigation, as the feedstock, lactose, does not depend on oil and has the potential of being from a renewable source.

The business case of paired electrosynthesis is very attractive and the technology ready to be implemented; however, it is crucial to extend in the next phase on experiments of the different production methods, based on electrolytic oxidation, of lactobionic acid and propylene oxide. Experimental data is needed to have a better understanding of the impact on the reactor performance data and to be able to achieve a successfully paired synthesis.

It is highly recommended to start-up a follow-up project so that the outcome can be tested in combination with Coval Energy's technology.

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## Introduction

Coval Energy and TU Delft are involved in a research program to reuse CO<sub>2</sub> for the production of formic acid, a valuable product. Formic acid has a relatively limited world market of about 1 million tons but has interesting potential as a carrier of hydrogen (H<sub>2</sub>) or carbon monoxide (CO) and as a supplier of carbon (C) for the chemical industry to displace fossil fuel sources. Formate or formic acid is directly produced by reducing CO<sub>2</sub> at a cathode of an electrolytic cell. The counter-reaction at the anode is the oxidation of water to oxygen. Both oxygen and formic acid are simultaneously produced in this process. Since oxygen does not have a high value, subject to local conditions, an alternative is sought for the anode reaction.

In general, it is worth noting that an electrochemical conversion has many benefits over traditional conversion processes, such as high functional group tolerance, mild conditions, and it is easy to scale at any size. With reference to the future increase of renewable energy, electricity as energy input enables that electrochemical synthesis is a logical next step towards a sustainable method for the synthesis of molecules.

The aim of this desk study is to review the literature to identify anodic electrochemical reactions that can produce specialty chemicals, paired with the cathodic electrosynthesis of formic acid. Therefore, two valuable products are simultaneously produced (i.e., a 200% electrosynthesis). The aim is to identify the technical feasibility of some interesting possible anodic oxidation reactions, which can be coupled with the reduction of carbon dioxide at the cathode. A design review will be performed on the expected impact of (a selection of) these chemicals on cell construction, like anode materials, membrane integrity, electrolytes, used materials, and feedstock and product transport. A limited market study will be performed.

## Specifications

In literature, electrosynthesis of many organic and inorganic chemicals has been identified.[1]–[3] Not all reactions are suitable for the purpose of this literature review due to the limitation of the paired electrosynthesis of formic acid. The following constraints are considered to identify the most promising electrochemical reactions without possible unwanted side effects on the reduction of carbon dioxide at the cathode:

- In the production of formic acid from carbon dioxide, a bipolar membrane is used. This means aqueous electrolytes are required for both cathode and anode sides. Other electrolytes such as ionic liquids cannot be used in this process, and both reactants and products should be soluble in water.
- The working temperatures range from 10 to 40 °C. This limitation is due to the short life of bipolar membranes at higher temperatures[4]. Therefore, neither cryogenic temperatures nor high-temperature processes are considered.
- Due to the continuous process, no solid or suspension phase can be introduced to the cell. This excludes all electrode-deposition reactions from this study.
- No pollution treatment systems are considered. This includes water treatment systems for removing dyes, medicines, and pesticides. This limitation is mainly due to the possible problems with the mass balance of cathodic and anodic streams.
- Due to the considerable number of organic electrosynthesis reactions, currently-available electrosynthesis processes are only considered.[5]

These criteria reduce the number of studies that have been carried out about electrosynthesis and define better the aim of this study. The final list can be seen in Appendices A and B. Many studies reported in this report were carried out at a laboratory scale. However, the performance of processes at laboratory operation conditions may be very different from the conditions for large scale applications. Therefore, the outcome of the reported studies (such as the operating conditions, current density, and current efficiency) should be tested and verified for the real process.[6]

## Electrosynthesis of Chemicals

This section consists of two parts for the electrosynthesis: inorganic and organic chemicals. The initial list of possible reactions was obtained from the review article by Sequeira and Santos.[5] The list of these inorganic and organic chemicals is provided in Appendix A and B. In the following subsections, initially, a list of potential chemicals is provided. These potential chemicals were chosen according to the criteria mentioned earlier. The electrosynthesis process for each chemical is then described.

### Inorganic chemicals

The list of inorganic chemicals studied in this review is summarized in Table 1.

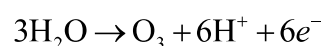
Table 1: List of studied inorganic chemicals

Number	Chemical
1	O <sub>3</sub> (ozone)
2	S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> (persulfate)
3	H <sub>2</sub> O <sub>2</sub> (hydrogen peroxide)
4	ClO <sub>4</sub> <sup>-</sup> (perchlorate)
5	ClO <sub>3</sub> <sup>-</sup> (chlorate)
6	Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> (dichromate)

### Ozone

Ozone has many applications in industry and specifically as a clean oxidant for water treatment. Other applications are industrial disinfection and sanitation (hospitals, food industry, etc.). Combined with its price of 0.05 USD/mol (2.3 USD/kg),[7] this is a good candidate for the pair electrosynthesis. There have been different ozone production methods such as corona discharge method[8] and ultraviolet light[9]. These methods use oxygen available in the air to cost-effectively produce ozone. This makes the yield of the process limited up to 6%. The alternative approach is to use electrochemical methods.

In an electrolytic cell, ozone is generated from the oxidation of water at the anode, from the following reaction:



This reaction competes with the oxygen evolution at the anode with a lower anodic potential (1.23 V vs. 1.51 V). The efficiency of ozone production depends on anodic materials, electrode morphology, cell configurations, current density, electrolyte, anodic potential, and temperature[10]. The ozone evolution is usually studied in acidic solution by using HClO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, HBF<sub>6</sub>, and HBF<sub>4</sub> as the electrolyte. The work of Wang and Chen[10] and Pushkarev[11] provides good reviews on electrolytic ozone generation. In these reviews, the anodic material is the main factor. With an anode made of Pt, the temperature usually ranges between -14 °C and -64 °C, up to 0 °C.[10] On a PbO<sub>2</sub> anode with a solid polymer electrolyte (Membrel), the conversion efficiency of 20% is achieved at a temperature of 30 °C and a current density of 1 A cm<sup>-2</sup>, with no sign of degradation after 2500 hour-operation.[12], [13] Between α-PbO<sub>2</sub> and β-PbO<sub>2</sub> crystals, the latter is preferred for the production of ozone[11]. Sb-doped tin dioxide coated on Ti electrode shows current efficiency as high as 15% in 0.1M HClO<sub>4</sub> solution at room temperature. By adding only 0.2% nickel to the coating solution to prepare nickel and antimony-doped tin oxide electrode (NATO), high current efficiency of over 30% was achieved;[14] sulfuric acid gives the highest current efficiency at or above 0.1 M acid concentration;[14] however, the lifetime of the anode is a problem due to the decay of current efficiency over time[10]. Boron-doped diamond electrode and an electrolyte-containing sulfuric acid could stably generate ozone with a high current density of 1 A cm<sup>-2</sup> and a current efficiency of a few percentages[15]. The boron-doped

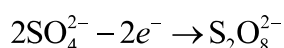


diamond anodes exhibit high activity and selectivity and good stability but require very high energy consumption for the process.

### Persulfate

Persulfate (i.e., Peroxodisulfate) is available in the form of three inorganic salts: ammonium persulfate ((NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>), potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>), and sodium persulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>). Nonetheless, persulfate anions are stable in purified water for several months[7]. More than 65% of persulfate produced is being used as a polymerization initiator. It has also been utilized in hair bleaches and lighteners, water treatment, soil and groundwater remediation, and etching of copper on circuit boards.[16] Persulfate (0.18 USD/mol; i.e., 0.74 USD/kg) is cheaper than other oxidants but it is more expensive than hydrogen peroxide (0.11 USD/mol; i.e., 1.5 USD/kg) for large-scale operations.[7]

At the commercial scale[17], persulfate is most commonly produced via oxidation of sulfate ions using platinum (Pt) or platinized titanium (Pt/Ti) electrodes at high current densities. At the anode, the following reaction produces persulfate:

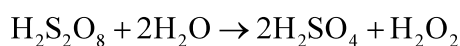


In the patents by Radimer and McCarthy,[17] and Lipsztajn,[18] the production of persulfate at high current densities are described at a platinum anode and a glassy carbon anode, respectively. The anolyte and catholyte are separated via a porous dielectric material and NAFION membrane, respectively. Cell potentials for these processes are between 7 V and 8 V, and 7 V and 15 V, respectively. The former process requires a minimum current density of 0.5 A cm<sup>-2</sup>, while the optimum current density of the latter ranges between 0.3 A cm<sup>-2</sup> and 1 A cm<sup>-2</sup>. For both processes, hydrogen is evolved at the cathode. The temperature ranges between 5 °C and 15 °C and it should remain below 40 °C. The high concentration of sulfate combined with a polarizer (e.g., fluoride) can considerably increase the current efficiency (as high as 90%).

Recently, the boron-doped diamond was suggested as the anode for persulfate electrosynthesis in a divided cell with ammonium sulfate as the electrolyte.[19], [20] According to the work of Zhu et al.,[20] a high current efficiency (93%) can be achieved in the initial stage (< 1 hour) at a current density of 0.15 A cm<sup>-2</sup>, which declines over time. Electrolysis under a constant current density of 0.15 A cm<sup>-2</sup> for 3 hours, yields approximately 0.74 M of persulfate from 100 mL of a mixed solution of 2 M H<sub>2</sub>SO<sub>4</sub> and 2 M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> at a current efficiency of 76%. The same level of productivity and current efficiency can be achieved using 4 M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> in the absence of added acid. The cell potential ranges between 4 and 6 V. Temperature is 15 °C. Hydrogen is produced at the cathode. In the work of Davis et al.[19], the effect of an aged electrode is studied. This effect decreases both the current efficiencies and anode potential (from 3-7 V to 2-5 V) for current densities up to 0.3 A cm<sup>-2</sup>.

### Hydrogen peroxide

Hydrogen peroxide has a vast industrial application in pulp and paper bleaching, disinfection, production of organic products, and cosmetic industries[21]. Hydrogen peroxide can be produced through two different paths: oxidation of sulfuric acid or partial reduction of oxygen. Due to the high cost of electricity (very high overpotential) and the cost of anodes (Pt or Pt-Ta-Ag electrodes) for the oxidation of persulfate, the focus of studies for the production of hydrogen peroxide is on the catalytic reduction of oxygen.[21] Nonetheless, hydrogen peroxide can be obtained from hydrolysis of H<sub>2</sub>S<sub>2</sub>O<sub>8</sub>: [21]



As mentioned earlier that persulfate is more expensive than hydrogen peroxide,[7] oxidation reaction may not be a proper choice for large-scale production of hydrogen peroxide.

### Perchlorate

Perchlorate ( $\text{ClO}_4^-$ ) have found industrial applications due to the strong oxidizing power[22]. Its salts are used as powerful oxidizing agents and as raw materials for rocket fuel[22]. Conventionally, perchlorate can be produced through the following 4 methods:[22] 1) Thermal decomposition of chlorates, 2) direct oxidation of sodium chlorate by strong oxidizing agents like persulfate, ozone, and lead dioxide, 3) reaction of a strong mineral acid chlorate and 4) neutralization of perchloric acid with an appropriate base.

The practical commercial production of perchlorate consists of three steps:[22]

- 1) Electrochemical production of sodium chlorate ( $\text{NaClO}_3$ ) from sodium chloride (see below[22])
- 2) Electrochemical oxidation of sodium chlorate to sodium perchlorate
- 3) Conversion of sodium perchlorate to other perchlorates

The second step can be performed at temperatures between 35 °C and 50 °C for current densities of 0.15-0.5  $\text{A cm}^{-2}$  in undivided cells.[21] The anode can be Pt/Ti,  $\text{PbO}_2/\text{Ti}$ , or  $\text{PbO}_2/\text{Graphite}$ .[21], [23] To obtain high current efficiency, the anode potential should be as large as possible because a high polarization enhances the chlorate oxidation rate more than the oxygen evolution. The cell potential is then between 5 and 6.5 V. Current efficiencies for platinum and lead dioxide anodes are 90-97% and 85%, respectively.[22]

In the work of Sánchez-Carretero et al.,[24] the application of boron-doped diamond anodes is investigated for the production of perchlorate from chloride salts. Perchlorate production efficiency improves by operating at high current densities and at alkaline conditions. Conversions of 100% to perchlorate can be achieved for a larger current charge passed.

### Chlorate

In large-scale production of perchlorate, chlorate is the raw material.[22] In addition, chlorate salts have industrial applications such as pulp and paper bleaching, herbicides, cotton and soybean defoliant, oxidizing agent, dye additive, textile dyeing, and metal etching.[22] The conventional method for production of chlorate is comprehensively described in the chapter "Chlorine Oxides and Chlorine Oxygen Acids" of Ullmann's Encyclopedia of Industrial Chemistry. In this process, an aqueous solution of sodium chloride is electrolyzed. Hydrogen and sodium hydroxide are formed at the cathode, while chloride is discharged at the anode. Chlorine does not evolve as a gas, but undergoes hydrolysis and produces hypochlorous acid ( $\text{HClO}$ ). Chlorate then forms simultaneously by two competing reactions: 1) predominantly by autoxidation of hypochlorite in the bulk electrolyte and 2) to a small extent (ca. 20%) by anodic chlorate formation. Different materials for the anode have been proposed. The operating conditions and performance of these systems for anodes with coatings of Pt/Ir/ $\text{RuO}_2$ , IMI, Platinite, Pt/Ir,  $\text{RuO}_2$ , Pt/Ir, Pt/Ir/ $\text{RuO}_2$ , and noble metal oxides are shown in table 12 of the chapter by Vogt et al.[22] Divided cells (unipolar, bipolar, and multipolar) are used. The cell potential ranges between 2.7 and 3.7 V with current densities between 0.15 and 0.35  $\text{A cm}^{-2}$ . The current efficiency of above 93% is achieved for all these systems. This is due to the introduction of stable metal anodes and efficient operation at high temperatures about 80-90 °C.[22] The minimum reported temperature in this list is 65 °C, which can be a drawback for the pair electrosynthesis of chlorate with formic acid at low temperatures.

## Dichromate

Dichromate is used in chemical, printing, textile, and pyrotechnics industries for applications such as oxidation of organic compounds, bleaching of montan waxes, and chromium complex dyes.[25] All chromium compounds can be synthesized starting from sodium dichromate ( $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ ). The conventional industrial process consists of three stages:[25] 1) Alkaline roast of chromite under oxidizing conditions, 2) leaching and 3) conversion of sodium monochromate to sodium dichromate by means of an acid. From sodium dichromate and sulfuric acid, chromic acid is often produced.

The electrosynthesis alternative to this industrial approach is the anodic oxidation of chromium(III) sulfate.[26] The system consists of several electrolytic divided cells with lead electrodes. At a current density of  $0.3 \text{ A cm}^{-2}$  and a cell voltage of 3.5 V, the current efficiency is 80%.[25], [26] The main disadvantage of this process is the high operating temperature of 95 to 100 °C.[26]

## Organic chemicals

The list of inorganic chemicals studied in this review is summarized in Table 2.

Table 2: List of studied organic chemicals

Number	Chemical	Starting material
1	Arabinose	Gluconate
2	gluconic acid (gluconate salts)	Glucose
3	Lactobionic acid (lactobionate salts)	Lactose
4	<i>p-t</i> -Butylbenzaldehyde	<i>p-t</i> -Butyltoluene
5	<i>p</i> -Methoxybenzaldehyde	<i>p</i> -Methoxytoluene
6	Propiolic acid	Propargyl alcohol
7	Erythritol	Glucose (starch/sugars)
8	Propylene oxide	Propylene

Note: in the previous version of this list, sorbitol was included. However, as glucose goes through cathodic reduction to produce sorbitol, it has been removed from this list. Also, the production of gluconate salts and gluconic acid is combined as in an aqueous solution at neutral pH, gluconic acid forms the gluconate ion, from which gluconate salts are produced.

### D-arabinose

D-arabinose is a monosaccharide, which plays an important role in the synthesis of vitamin B2 and DNA. Conventionally, D-arabinose is produced via Wohl (or Ruff-Fenton) degradation. In this process, calcium oxidized by means of hydrogen peroxide in the presence of ferric acetate.[27]–[29]

The alternative electrosynthesis of D-arabinose is the direct degradation oxidation of the salts of D-gluconic acid. According to the patent by Jiricny et al., [30] this process is carried out with the aid of the fluidized bed anode and a layer of electrically conductive particles (e.g., coke and graphite). The anolyte is separated from the catholyte via a porous membrane. The temperature is 40 °C. At a current density of 0.119 A cm<sup>-2</sup>, a mass conversion of 78.9% is obtained. In the work of Vallières and Matlosz,[31] this electrosynthesis process is studied in a multisectioned flow-through porous electrode. In the work of Chou and Chou,[32] the pair electrosynthesis of arabinose on both electrodes is studied. An H-type divided glass cell is used, and the temperature is kept fixed at 70 °C. The maximum current efficiency of 85% is achieved for anodic oxidation while the current efficiency of cathodic reduction to produce arabinose is reported to be not sufficient. The current density in this experiment is rather small and limited to 0.01 A cm<sup>-2</sup>.

### Gluconic acid (gluconate)

Gluconic acid is a natural constituent in fruits and honey, it has found applications in the food industry for the prevention of milk stone in the dairy industry or cleaning of aluminum cans. Its salts are also used in the formulation of food, pharmaceutical and hygienic products such as calcium therapy and animal nutrition.[33] According to Sumitra et al.,[33] its worldwide annual production is 60,000 tonnes as a 50% mass aqueous solution. Gluconic acid is produced from glucose through a simple dehydrogenation reaction catalyzed by glucose oxidase. There are different approaches available for the production of gluconic acid: chemical, electrochemical, biochemical, and fermentation processes. Current commercial production of sodium gluconate uses fermentation with *Aspergillus niger* at a temperature of 34 °C and a pH of 6.0-6.5.[33]

Gluconic acid and its salts can also be produced in an electrolytic cell. In 1932, Isbell et al.[34] described the electrosynthesis of calcium gluconate from dextrose. More recent studies have focused on pair electrosynthesis of gluconate and sorbitol in an undivided cell from anodic oxidation and cathodic reduction of glucose, respectively. According to the work of Park et al.,[35] the optimum operating

conditions for the paired syntheses is at a temperature of 60 °C with a current efficiency of >99%. At a temperature of 25 °C, the current efficiency decreases to values above 70%. The anolyte consists of 1.6 M glucose and 0.4 M CaBr<sub>2</sub> with a pH 5-7, and the cathode is graphite. The cell potential ranges between 2.2 and 3.5 V, depending on the cathode used in the cell. In the work of Li et al.,[36] a similar process is studied but with a dimension stable anode (DSA) in a press filtration diaphragm cell. The anolyte is 66.7% glucose and 2% NaBr. This process operates at a temperature of 60 °C, the current density of 0.050 A cm<sup>-2</sup>, cell potential of 4.1 V, and current efficiencies above 80%.

#### Lactobionic acid (lactobionate)

Lactobionic acid and its salts have a diverse range of applications in pharmaceutical, food, chemical, cosmetic, and nanotechnology industries owing to its antioxidant, chelating, humectant and emulsifying properties. These applications are thoroughly described in the review by Gutiérrez et al.[37] The most important commercial usage is as a major ingredient of the cold-storage solutions employed for stabilizing organs prior to transplantation.

The selective conversion of lactose to lactobionic acid consists of the oxidation of the free aldehyde group of glucose on the lactose molecule to the carboxyl group.[37] Several industrial processes are currently available for the production of lactobionic acid: electrochemical, biocatalytic and heterogeneous catalytic oxidations. All these processes are comprehensively reviewed by Gutiérrez et al.[37]

In 1934, Isbell patented the process for electrosynthesis of calcium lactobionate from lactose in the presence of bromine and calcium carbonate, using graphite electrodes.[38] This process was improved by Magariello and Isip,[39] who patented a method for a large-quantity production by electrolytic oxidation of lactose with a yield of 98%. They used iodine or bromine as catalysts, and an alkaline solution to maintain the pH above 5. In the work of Druliolle et al.,[40]–[43] high yields (>90%) and selectivities (100%) could be obtained at ambient temperatures (25 °C) by means of the electrocatalytic oxidation of lactose on noble metal electrodes (platinum, platinum-modified and gold electrodes) in alkaline media. An ion-exchange membrane is used. In these studies, the current densities are limited to several mA cm<sup>-2</sup>, with a maximum value of 4 mA cm<sup>-2</sup>. These authors also proposed that gold electrodes could be the best catalyst for the oxidation of sugars, and that lactone is the primary product of the electrochemical oxidation of lactose, which is hydrolyzed in a subsequent step to produce lactobionic acid, following a similar mechanism to that of glucose.

#### *p*-*t*-Butylbenzaldehyde

*p*-*t*-butylbenzaldehyde (TBBZ) is used as an intermediate for the production of medicines, agricultural pesticides, and perfumes (Lilial).[44] Traditionally, the compound is produced from 4-*tert*-butyltoluene by homogeneous oxidation in acetic acid solvent catalyzed by soluble acetates of transition metals, but both conversion and selectivity are unsatisfactory, and separation of metal catalysts is difficult.[44] 4-*t*-butylbenzaldehyde can also be synthesized by oxidation of 4-*t*-butyltoluene using MnO<sub>2</sub> in concentrated sulfuric acid.[45] However, using stoichiometric quantities of MnO<sub>2</sub> produces large quantities of MnSO<sub>4</sub> which is not only expensive but also a waste disposal problem.[45]

In the patent by Degner et al.,[46] the preparation of 4-*tert*-butylbenzaldehyde by electrochemical oxidation of 4-*tert*-butyltoluene is presented in the presence of inorganic acid and an alkylsulfonic, alkenylsulfonic or arylsulfonic acid. Suitable anode materials are lead oxide and titanium coated with lead dioxide. At current densities from 0.01 to 0.1 A cm<sup>-2</sup> and temperatures between 10 and 90 °C, the conversion rate of 10% to 50% can be achieved in a cell divided by a cation exchange membrane. In the work of Tissot et al.,[47] this electrosynthesis process is studied for several anode materials studied; Pb-Sb alloys give the best yields of *p*-*t*-butylbenzaldehyde at 60 °C and current density of 0.04

A  $\text{cm}^{-2}$  in 1 M  $\text{H}_2\text{SO}_4$ . In the work of Vaze et al.,[48] the effect of operating conditions is studied. Low acid concentrations in the electrolyte and lower operating temperature favor high current efficiency. Zollinger et al. studied the electrooxidation of p-t-butyltoluene in a methanol electrolyte containing sulfuric acid and water at a boron-doped diamond or graphite anode, coupled with hydrogen production at the cathode.[49] The experiments were conducted under galvanostatic conditions at  $0.034 \text{ A cm}^{-2}$ , cell potentials between 4 V and 9 V, and a temperature of  $54 \text{ }^\circ\text{C}$ .

Because of the poor solubility of p-t-butyltoluene in aqueous electrolyte,[48] electrolysis should be carried out using an emulsion of p-t-butyltoluene in the electrolyte containing sulfuric acid or methanol. This requires an aqueous solution of these chemicals as the electrolyte for the electrosynthesis process. However, according to the work of Kim et al.,[50] the addition of water reduces the current efficiency for the side-chain oxidation of p-t-butyltoluene.

#### *p*-Methoxybenzaldehyde

p-methoxybenzaldehyde is a natural constituent of some etheric oils and is used as a flavor component of soaps and other cosmetics and as an intermediate for the synthesis of some pharmaceuticals. In addition, it can be used as a corrosion inhibitor and electroplating brightener.[51] As also mentioned for p-t-butylbenzaldehyde, substituted benzaldehydes are normally synthesized from the corresponding toluenes in the liquid phase in the presence of Co, Ce and Mn salts in acetic acid medium or by electrochemical methods.[52]

Lodowicks and Beck study batch-type electrosynthesis of p-methoxybenzaldehyde from p-methoxytoluene in a divided electrolytic cell.[53] The solvent/anolyte system is 1 M  $\text{H}_2\text{SO}_4$ /5M  $\text{H}_2\text{O}$  in methanol with activated titanium anodes and a spinel coating of  $\text{CoMn}_2\text{O}_4$  of about  $1 \text{ }\mu\text{m}$  thickness as the anode. The temperature and current density are set to  $23 \text{ }^\circ\text{C}$  and  $2.5 \text{ mA cm}^{-2}$ , respectively. Optimum results (50% to 60% current efficiency) were obtained at low concentrations of p-methoxytoluene (0.2M). A part of the current is consumed for the formation of benzylmethylether. In the work of Jiang et al.,[51] the electrooxidation of p-methoxytoluene at the graphite/Nafion composite electrodes is investigated. p-Methoxybenzaldehyde and a small amount of p-methoxybenzoic acid are obtained. Regarding a higher current efficiency,  $\text{Ce}^{3+}$ -Nafion membrane performs up to 20% better than  $\text{H}^+$ -Nafion membrane at low current densities (more than  $5 \text{ mA cm}^{-2}$  and less than  $30 \text{ mA cm}^{-2}$ ). However, both types of the membrane can provide a current efficiency of 88% at a current density of  $2.5 \text{ mA cm}^{-2}$ .

#### Propiolic acid

Propiolic acid is used as a laboratory reagent for the synthesis of transition metal complexes, haloalkyl propiolates, and halopropenoates.[54] In addition, it has found applications in agriculture and in the control of nematodes.[55] This chemical is produced by oxidizing propargyl alcohol at a lead dioxide/titanium composite anode in the presence of sulfuric acid.[55], [56] In the patent and the article by Nohe et al.,[56], [57] this electrosynthesis process is explained in a divided cell with a cation exchange membrane. Anolyte can consist of between 2%wt. and 12%wt. propargyl alcohol with different concentrations of sulfuric acid. At temperatures below  $30 \text{ }^\circ\text{C}$ , current densities up to  $0.25 \text{ A cm}^{-2}$  can be obtained. At a temperature of  $25 \text{ }^\circ\text{C}$ , cell potentials of 2.9 V and 3.3 V are obtained for current densities of  $0.10 \text{ A cm}^{-2}$  and  $0.20 \text{ A cm}^{-2}$ , respectively. The propiolic acid can be extracted from the electrolyte containing sulfuric acid by using an ether which contains more than one ether oxygen atom and boils above propiolic acid and at temperatures between  $0 \text{ }^\circ\text{C}$  and  $50 \text{ }^\circ\text{C}$ .

More recent studies have focused mainly on the electrooxidation of propargyl alcohol to other products rather than propiolic acid.[58], [59]

## Erythritol

Erythritol is used in industry as a food additive and recently as a phase-change material (PCM) constituent.[60], [61] The current main application is in the food industry and as a natural sweetener in products such as sugar substitute, hard candy, chewing gum, fruit novelty snacks, ready-to-eat cereals, cakes, baking mixes, non-dairy toppings.[60] It is a suitable substitute for table sugar without adverse effects on tooth or blood sugar and insulin levels. Erythritol is industrially manufactured through fermentation of a simple sugar solution, such as glucose or sucrose, using a pure culture of yeast, *Moniliella pollinis*.[60], [62] The currently-high retail price discourages consumers from common consumption, despite Erythritol's enormous advantages over table sugar. Therefore, numerous studies to improve the bio-synthesis of erythritol have been reported.[62]

In the current decade, a green electrochemical process has been developed by Dynamic Food Ingredients (DFI) Corporation for a cost-effective production of erythritol at a large scale.[63] In the patents by Stapley et al.,[64]–[67] the electrosynthesis process developed by DFI Corp is described and consists of several steps (shown in Figure 1). This process consists of two oxidation (decarboxylation) reactions to produce erythrose from either D-ribonic acid or D-arabinonic acid, and produce these acids from sugars. Erythrose is then reduced to produce erythritol. The focus of these patents is rather on the step for electrochemical decarboxylation of a carbohydrate acid to erythrose. This process can be performed at ambient temperatures, in continuous or batch mode, and in a divided or an undivided cell. In Example 1 of the patent by Stapley et al.[65] electrochemical decarboxylation of arabinonic acid is described. The anode is made of graphite foil. At a current density of  $0.1 \text{ A cm}^{-2}$ , an average cell potential of 6.5 V, and ambient temperature, erythrose is produced. This erythrose is chemically reduced with an excess amount of sodium borohydride to produce erythritol with a yield of 81.1%. In Example 1 of the patent by Genders and Stapley,[67] the paired synthesis of erythrose from arabinonic acid (anode) and erythritol from erythrose (cathode) is described in a three-compartment Microflow cell. This comprises a carbon anode, at cation exchange membrane a bipolar membrane, and a cathode (Ru onto Ni substrate). At a constant current density of  $0.150 \text{ A cm}^{-2}$ , the current efficiencies for arabinonic acid oxidation and erythrose reduction are 87% and 73%, respectively.

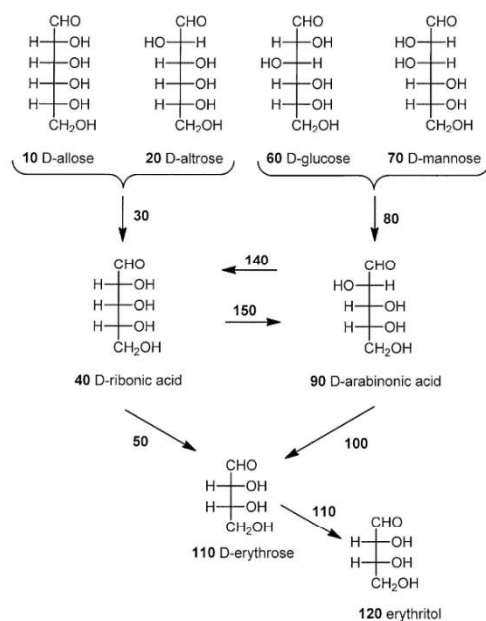


Figure 1: Reaction scheme showing reaction steps using certain allose, altrose, glucose or mannose starting materials[65]

## Propylene oxide

Propylene oxide (or propene oxide) is an important basic chemical intermediate and it is mainly used to produce polyether polyols (flexible/rigid foams), propylene glycols, and propylene glycol ethers as well as other non-foam uses.[68] Therefore, propylene oxide is used as a raw material for major consumer goods in virtually all industrialized countries with several million-tonne annual production[68]. The selection of production routes is decisively influenced by the application and market potential of coproducts, as well as by the availability of raw materials and possibilities for byproduct management. The 5 major industrial routes for the production of propylene oxide from propene are shown in Figure II. More information about these industrial routes can be found in the work of Baer et al.[68] and Nijhuis et al.[69]

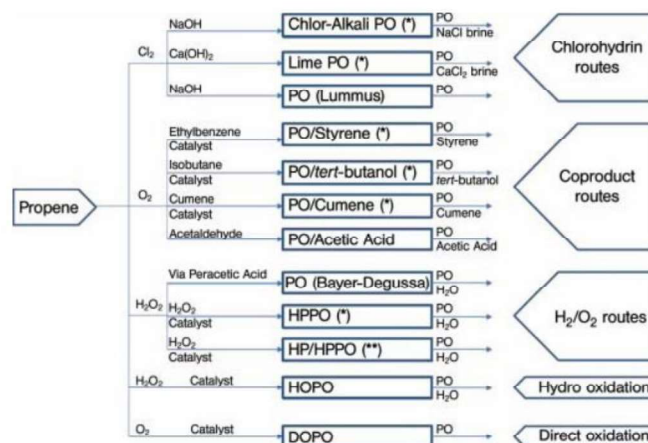


Figure II: Summary of propylene oxide production routes.[68] PO stands for propylene oxide.

Other alternatives such as electrosynthesis routes have been proposed, but they are not currently applied on an industrial scale.[68] In the work of Ellis and Jansson,[70] and Manji and Oloman,[71] the synthesis of propylene oxide by electrolysis of dilute sodium bromide solution with propylene gas is investigated in an electrochemical 'flow-by' bipolar reactor consisting of six parallel fixed beds of graphite particles separated by polypropylene felt diaphragms. The reaction scheme for this process is shown in Figure III.

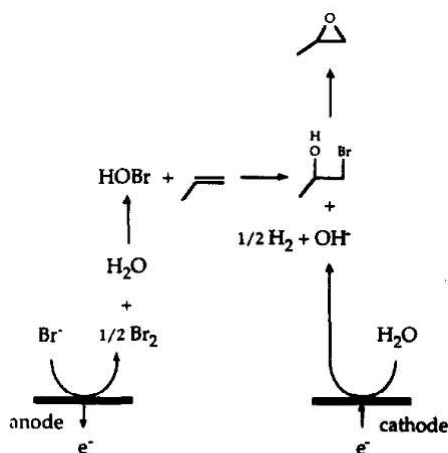


Figure III: Reaction scheme for propylene epoxidation[72]



Different operating conditions such as current density (0.04-0.27 A cm<sup>-2</sup>), sodium bromide concentration (0.2 M and 0.5 M), propylene gas load (0.08-1.66 kg m<sup>-2</sup> s<sup>-1</sup>), reactor temperature (30 and 60 °C) are investigated. The maximum absolute pressure is 2.2 atm. Depending on the conditions, the current efficiency and the specific energy consumption vary from 14% to 58% and from 6 to 60 kWh kg<sup>-1</sup> of propylene oxide, respectively. The low current efficiency and high specific energy is largely accounted for by current bypass and losses due to the secondary generation of bromate, oxygen, and dibromopropane as well as possible losses of intermediate bromine species of cathodic reduction.[71] In the work of Belmont and Gault,[72] the optimum cell potential is set between 3 and 4 V in such a way that the rate of bromine formation is high enough to allow a consequent production of propylene oxide but low enough to avoid the formation of bromate. The optimum temperature is between 6 °C and 10 °C. Under these conditions, a current efficiency of 68% and energy consumption of 2.0 kWh kg<sup>-1</sup> can be achieved.

#### Concluding remarks from the Literature study

In this literature study, possible anodic electrooxidation reactions were considered to produce specialty chemicals instead of oxygen, paired to the electrosynthesis of formic acid at the cathode. Two groups of products were considered: Inorganic and organic chemicals.

From the list of inorganic products considered here, ozone (O<sub>3</sub>) and persulfate (S<sub>2</sub>O<sub>8</sub><sup>2-</sup>) are the most promising specialty chemicals. Both have a high value with a large number of industrial applications. Hydrogen peroxide production via cathodic reduction is commercially more favorable since the raw material for the anodic oxidation is persulfate. The main disadvantage of electrosynthesis of chlorate and dichromate is high operating temperatures (80-100 °C). Production of perchlorate requires chlorate as the starting material and its application is limited compared to chlorate, chlorite, hypochlorite, or chloride compounds.

The most promising organic chemicals are propiolic acid and propylene oxide, which are produced from propargyl alcohol and propylene, respectively. These chemicals can be electro synthesized at rather low (ambient) temperatures and rather high current densities. The drawback of propiolic acid is that it is severely toxic, and even reported as fatal, causes severe skin burns and eye irritation and is highly flammable {Echa documentation}. The route to produce lactobionic acid from lactose has a low current density at present, but it might be a promising candidate after further investigation, as the feedstock, lactose, does not depend on oil. The product lactobionic acid is a valuable chemical as well. Erythritol can be another potential candidate, which can be electro synthesized from simple sugars, but the whole process consists of several reaction steps. This can make it difficult to make a pair synthesis with a reduction of CO<sub>2</sub>. D-arabinose requires high operating temperature (70 °C). The current density for electrosynthesis of lactobionic acid is very small and in most recent studies is limited to few mA cm<sup>-2</sup>. The main issue with the production of benzaldehyde and its derivatives is the low solubility of these chemicals in water, which requires highly concentrated solutions of methanol or sulfuric acid and considerably low concentrations of water. Nonetheless, it should be noted that it is possible to make solutions to insoluble chemicals in water by adding cosolvents to the electrolyte. This can be considered for all insoluble chemicals that were not studied here.

## Constructability and design review.

### Current stack design

The current design of the Coval Energy reactor is based on a two-compartment stacked electrochemical cell that can be operated up to 100 bar. The compartments are separated using a bipolar membrane (BPM). Up to ten complete cells can be stacked.

Currently, two different brands of bipolar membranes have been used.

- Fumatech Fumasep FBM-PK, a PEEK reinforced membrane of 130-micron thickness
- Membrain, Ralex BM, the thickness of 0.4 mm

The volume of one electrochemical cell the cathodic compartment is 10 mL, and the anodic compartment is 10 mL. Both electrodes are made out of metal slabs.

Cathode material:

- Tin-based alloy (Coval Energy) cathode with a reactive surface area of 100 cm<sup>2</sup>

Anode material:

- Iridium mixed metal oxide (Ir-MMO, Magneto Special Anodes) anode with a surface area of 100 cm<sup>2</sup>

The reactor is designed to be operated at room temperature, so no high temperatures are required.

So far, the design and optimization efforts of the electrochemical reactor were mainly focused on the cathode side synthesis. Although the anode side has a significant influence on the performance of the BPM. As such, an aqueous electrolyte is required at the anode side. Therefore both reactants and products should be soluble in water.

The Key Performance metrics for an electrochemical cell are Faradaic Efficiency (FE), and Current Density (CD). The FE is an indication of the selectivity of charge transfer in an electrochemical reaction towards the desired product. The CD is equivalent to the rate of reaction, knowing that the BPM is limited by its materials used (permeability, stability, etc.), and catalysts are required to reduce the electric potential of a bipolar membrane and thereby the activation energy for the overall dissociation reaction. The CD of the used BPM's is in the range up to 200 mA cm<sup>-2</sup>. Between the cathode and BPM and a spacer is applied to prevent direct contact of the BPM with the cathode, and that the aqueous electrolyte can permeate into the BPM. At the Anode compartment also a spacer is applied to provide a functional contact area with the aqueous electrolyte with the BPM contact area. See figure IV for an overview of the electrochemical reactor.

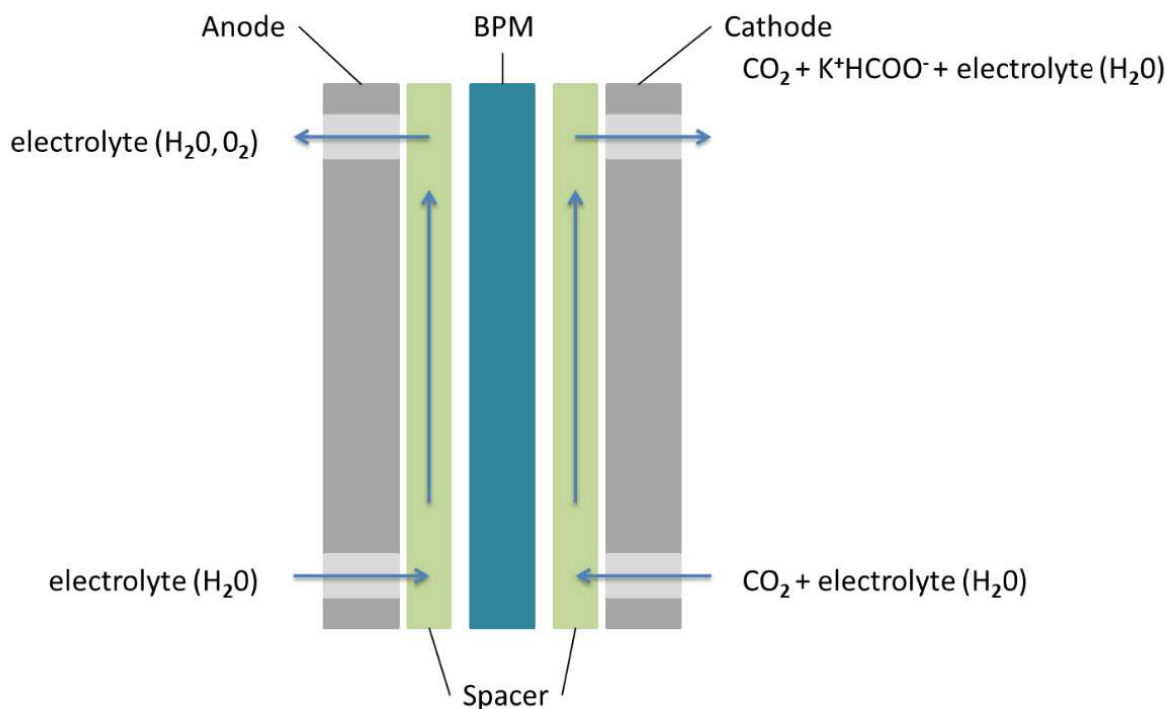


Figure IVV: Reactor scheme

The efficiency of the reaction of CO<sub>2</sub> to formate or formic acid, depending on the pH of the electrolyte, depends on two main parameters: the availability of CO<sub>2</sub> near the electrode and the potential. The availability of CO<sub>2</sub> can be influenced by the pressure and the residence time of the electrolyte at the cathode side. In general, a higher pressure leads to a higher solubility of CO<sub>2</sub>. If 0.5 M KHCO<sub>3</sub> is used as an electrolyte, the solubility of CO<sub>2</sub> increases by a factor of 3 between 1 and 50 bar. The flux of CO<sub>2</sub> molecules to the cathode is influenced roughly by the reaction rate and the diffusion of CO<sub>2</sub>. A model to describe this has been developed by A.R.T. Morrison et.al.[73] It is known that a tin-based electrode selectively reduces CO<sub>2</sub> at low overpotential. In the case of this reactor, a cell potential between 3 and 3.5 volt is optimal. At 4-4.5 volt, the hydrogen evolution reaction becomes more efficient than the CO<sub>2</sub> reduction reaction. [74]

### Reaction selection

Two different types of products have been investigated in the literature study: inorganic and organic products.

Most of the inorganic oxidation reactions need a large overpotential. Therefore, these reactions cannot be coupled to the formic acid formation on a tin-based electrode, because the CO<sub>2</sub> reduction reaction requires a low overpotential.

The most promising organic oxidation reactions are the production of propylene oxide, an epoxide, and oxidation of various sugars. To our opinion, the production of propylene oxide is most beneficial in the short term. Propene is not available (yet) as a renewable feedstock, but is produced from fossil fuels. However, in the short term, the electrochemical oxidation of propene to propylene oxide can contribute to the electrification of the chemical industry and lead to lower CO<sub>2</sub> emission. In the long term, the electro-oxidation of sugars will be the direction to go to, as sugars are obtained from biomass. For example, lactose is a constituent of milk. Glucose can be obtained from a lot of different sources, amongst them is cellulose. Of the different sugar oxidation processes described in the

literature review, gluconic acid and lactobionic acid seem to be the most viable. The other sugar-based products, arabinose and erythrol, are more complicated to implement due to either a large number of reaction steps or the production method.

At present, the electro-oxidation of propylene oxide is easier to implement commercially. But as electro-oxidation of sugars is the best solution for the long term, both routes are selected for a design review/case study. The other identified molecules are too far from the current stack design, and therefore, it will be more useful to choose a molecule synthesis that can be applied in the contemporary design of the Coval Energy reactor configuration.

### Case study: propylene oxide

#### State of the art

Currently, researchers have converted propene to propylene oxide at atmospheric pressure and at temperatures between 0 and 15 degrees centigrade. This was done with a two-step synthesis. In the electrochemical reactor, the double bond is opened by adding an OH group and a bromine atom on a platinum-coated electrode. After the opening of the double bond, the epoxide is formed in a separate step by the removal of the hydrogen atom of the OH group with an OH<sup>-</sup> atom. According to Belmont et al, [72], the optimum potential for this reaction is between 3 and 4 volts. The obtained current efficiency was 68%, with a production of 0.12 mol / (h\*dm<sup>2</sup>). The reaction scheme for this process is already shown in Figure III and in figure V the potential reaction is shown in the current stack configuration.

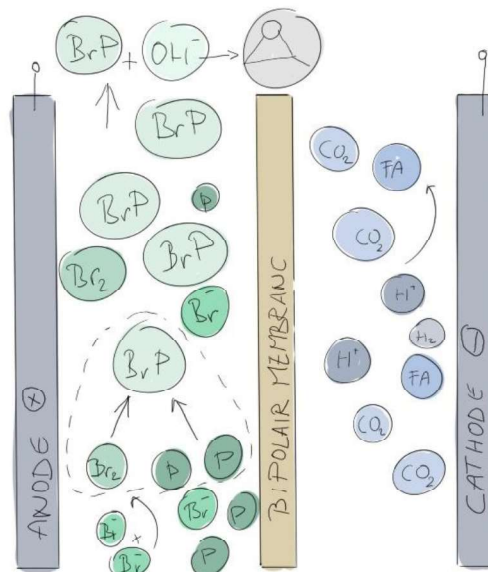


Figure V: Reaction scheme showing the paired synthesis of PO

#### Integration in current stack design

The main difference between the experimental conditions described in the literature and the current stack is the difference in pressure. However, as the solubility of propene increases with increasing pressure, this difference works in our favour. Special attention should be paid to the dissolution of propene in the electrolyte. At room temperature, the vapour pressure of propene is around 10 bar. This means that it is a liquid at the current reaction conditions of the formic acid reactor. In general, the liquid-liquid phase equilibria take longer equilibration than gas-liquid equilibria. Moreover, the liquid density of propylene is only half of the liquid density of water. This means that some kind of

mixing is required to enhance the mass transfer of propene to the electrolyte. If liquid propene is directly fed into the electrolysis cell, countercurrent flow, with propene added from the bottom, might be applied.

Currently, the formation of propylene oxide is tested in an undivided cell. This should not create any problem, as the reaction is only taking place at the anode and no products of the cathode are involved in the reaction. In the current stack design, a bipolar membrane is used, consisting of an anion exchange membrane and cation exchange membrane glued together, in some cases by using a reinforcement layer. A benefit of using a BPM membrane is that water splitting takes place at the AEM/CEM interface. OH<sup>-</sup> ions are formed at the anode side and H<sup>+</sup> ions at the cathode side. OH<sup>-</sup> ions are needed for closing the epoxide ring. As now the two steps can take place in the same reaction vessel, this might enhance the current efficiency as well. Currently, the formation of OH<sup>-</sup> ions is a byproduct of the purification setup for the formic acid. This can be used as an additional source for the reaction towards the epoxide.

Downstream separation of propene oxide is quite easy. It is soluble in water. With decreasing the pressure, propene can be removed from the product stream. Propylene oxide might be separated from water by distillation, as the boiling point of propylene oxide is 34 °C.

#### Materials

The extra materials needed for this reaction are a Platinum-coated electrode, a mixing unit and a heat exchanger. All those materials are readily available. Magneto developed a Platinum coated titanium electrode, with special attention to the Pt on Ti connective layers. As a rough number, the Pt electrode will cost 2200-2500 €/ m<sup>2</sup>. The titanium must be coated completely, including the holes, as bromide attacks titanium.

#### Economics

Propylene oxide is an organic compound used for the production of polyether polyols that acts as a building block in the formation of polyurethane plastics. Polyether polyols are produced by the ring-opening polymerization of propylene oxide and a compound containing two or more active hydrogen atoms called the initiator. Other epoxide monomers such as ethylene and 1,2-butylene oxides are also used. There is also a wide range of products for polyols, e.g., coatings, thermoplastic resins, fibers, adhesives, and sealants.

Mainly due to the increasing demand for polyurethane across the globe, polyether polyols segment of the propylene oxide market has the most significant share in the market. Asia Pacific region has the most significant size in the propylene oxide market. The Asia Pacific region has an increasing demand for propylene oxide from textile & furnishing, building & construction, and packaging industry. The propylene oxide market is projected to reach \$20 Billion by 2024 according to several Markert reports.

In summary Propene → Propylene oxide pros and cons

Pros:

- Moderate current density (100-200 mA.cm<sup>-2</sup>) (in the range of FA production)
- Large global market (large volume possible)
- Local commodity market in the Netherlands and Germany (local off-takers)
- The electrochemical production cost price in the range of the added value, see market prices (Propylene Oxide ~\$1750/t, propene ~\$1300/t)

Cons:

- Large modification to the reactor setup (higher CAPEX)
- The conductivity of anolyte might be lower (lower FA production)
- Downstream purification might be more complex (higher CAPEX)
- No large scale production experience with propene to propylene oxide yet (higher CAPEX)
- Additional bromine electrolyte needed

## Case Study: Valuable chemicals from sugars

### State of the art

Both gluconic acid and lactobionic acid can be obtained by electrocatalytic oxidation using a noble method cathode. Platinum and gold are often used. The newest research makes use of (bi-)metallic nanoparticles immobilised on conductive support like Vulcan carbon black. This support is subsequently impregnated on carbon felt, a conductive carbon electrode. With the help of a semi-permeable layer, like nafion, the nanoparticles on support are immobilized on the carbon felt, to prevent leaking of the catalytic material in the electrolyte. Another route is the use of gold- or platinum-coated titanium. Of all the materials tested, gold or a bi-metallic catalyst containing gold and platinum works best.

Most research is performed in H-cells, or with a special type of electrodes like rotating disk electrodes. Research using flow cells is hardly executed.

The typical cell potential used for sugar oxidation is between 2 and 3.5 volt, comparable with the current cell potential used for the formation of formic acid, which is 3-3.5 volt. Especially the reaction of lactose to lactobionic acid can benefit from elevated temperatures during the reaction: the current efficiency gets higher with increasing temperature. However, the researchers found a respectable current efficiency at 25 °C. The current density used for the reaction is currently quite low, in the order of a few mA.cm<sup>-2</sup>. The conversion of lactose to lactobionic acid in the paired setup is presented in figure VI.

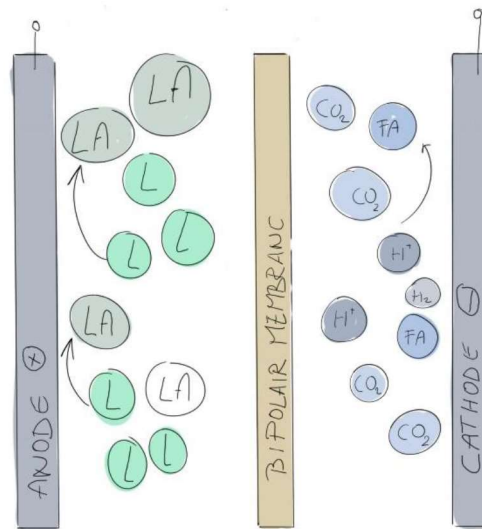


Figure VI: Reaction scheme showing the paired synthesis of LA

### Integration in current stack design

As the electrode of choice, coated metal should be used. Carbon felt can be quite brittle and unstable. When closing the current reactor design stack, quite some force is needed to make it leak-tight. We expect that carbon felt is likely to break during this procedure. Special attention should be paid to flow cell experiments, as those have not been performed, to our knowledge. This means that first, a couple of basic flow cell experiments should be executed, to determine the optimum cell voltage for the co-production of the two products and the optimum concentration. We feel that it still has added value to use a bpm membrane, as that will slow down the crossover of K<sup>+</sup> ions from the anode to the cathode compartment. Although the elevated temperature is beneficial for the current efficiency of the

reaction of the sugars, it is better to perform the reaction at room temperature if it is co-produced with formic acid. First of all, the membrane is sensitive to heat, and second, the CO<sub>2</sub> solubility will decrease with increasing temperature.

The downstream processing, however, will be complicated, as the products all dissolve in water. Something like chromatography might be needed as a separation method.

### Materials

The extra materials needed to perform this reaction in our current design are the precious metal coated electrodes. Gold is the material of choice. These electrodes are made commercially. We expect the price to be similar to that of the platinum electrodes, 2200-2500 €/m<sup>2</sup>. The other elements are all similar. No additional mixing is required, as lactose and glucose are both soluble in water.

### Economics

The global lactobionic acid market is highly consolidated. Major players control more than 60% of the market and have a presence in regional and global markets. The current market players are Sandoz, Cayman, Merck Group, Bio-sugars, Wu Xi Sigma Chemical Products, and Reliable Biopharmaceuticals.

The growth rate of global consumption is smooth. Europe is one of the main consumption regions due to the advanced production technology and rapid development of the economy. The major raw material for lactobionic acid is lactose. On the global market, the market price of lactose is volatile. As such, the fluctuations in the price of the upstream product will impact the production cost of lactobionic acid. Several market reports predicted that the consumption increasing degree would show a smooth growth curve. For product prices, the slow downward trend in recent years will maintain in the future as competition intensifies. Besides, prices gap between different brands will go narrowing gradually. Also, there will be fluctuation in gross margin. Global Lactobionic Acid market size will increase to 18 Million US\$ by 2025.

The current price of Lactobionic Acid ≥95% is ranging from 20 – 100 € per kg.

The current price of Lactose is ranging from 2 - 20 € per kg

In summary Lactose → lactobionic acid pros and cons

Pros:

- Local commodity market in the Netherlands (local off-takers)
- The electrochemical marginal production cost is not the main cost items
- Good understanding of the electrochemical production process

Cons:

- Large modification to the reactor setup to be incorporated (higher CAPEX)
- Low current density (2 - 4 mA.cm<sup>-2</sup>)
- The conductivity of anolyte might be lower (lower FA production)
- No large market potential
- Additional electrolytes and reactor modifications are needed.



## Business case

A limited market study has been performed to identify prices, volumes, competing technologies and competitors for the selected chemicals. Combined with the results of work packages 1 and 2 a concluding report will be made on the profitability of the selected chemicals.

### The current Business case for FA

Based on the current reactor performance (cell potential 3.2V and a CE of 80%), the electrochemical production of FA will be based on a marginal cost price of 380€/t (including purification). The FA market value of FA ranges between 450€/t up to 800 €/t. As such, there is some margin-left for the CAPEX. The underpinning figures for the FA production costs are listed in Table I and Table II:

*Table I of consumable to produce 1 t FA*

Input data Coval reactor		
Production of formate/FA	[t/year]	1,0
CO <sub>2</sub>	[t/year]	1,3
Electricity	[MWh/year]	7,3
Water make-up	[m <sup>3</sup> /year]	0,5
KOH surplus	[t/year]	0,05

The corresponding prices for the used consumables are listed in table x.x

*Table II cost price consumables.*

Cost prices		
CO <sub>2</sub>	[€/t]	10
Electricity (renewable)	[€/MWh]	40
Water	[€/m <sup>3</sup> ]	6
KOH	[€/t]	800

### The potential business case for paired production of FA and PO

The marginal production cost of FA production will be impacted by an increase of ohmic losses due to the lower conductivity of the anolyte and a lower production rate due to a lower CE. Also, an additional amount of bromine material will be needed: As such the following guesstimation has been used, presented in Table III :

*Table III with the paired reactor case*

Production of formate/FA	[t/year]	1,0
Production of PO	[t/year]	0,6
CO <sub>2</sub>	[t/year]	1,7
Electricity	[MWh/year]	8,1
Water make-up	[m <sup>3</sup> /year]	0,7
KOH surplus	[t/year]	0,05
Bromine surplus	[t/year]	0,08
Paired reactor performance		
Current efficiency	[%]	60%
Cell voltage	[V]	4,2

Including the purification step, the marginal production cost of FA will be impacted and will be increased up to a marginal cost price of 560 €/t. However, the added value of this paired syntheses is approx. 200 €/t of PO produced. Therefore the FA marginal production cost might be slightly improved. It is worth mentioning that the cost of downstream purification of the PO has not been taken into account.

Conclusively the business case for the paired syntheses option of FA and PO seems to be marginally improved. More experiments are needed to obtain a better understanding of the reaction mechanisms, the performance impact, reactor modification requirements, and PO purification requirements.

### The potential business case for paired production of FA and lactobionic acid

The production of lactose by electrolytic oxidation is very selective. However, the current density used for the reaction is currently quite very low. Several studies reported that current densities are limited to several mA cm<sup>-2</sup>, with a maximum value of 4 mA cm<sup>-2</sup>. As such, the reported quantity production rates by electrolytic oxidation of lactose with a yield of 98% is difficult to be accommodated in the current setup of the COVAL reactor. The FA production will be in the range of 150 mA.cm<sup>-2</sup>, which is currently a significant miss-match with the production rates of Formic Acid. Nevertheless, assuming that the paired electrochemical production of lactobionic acid takes place at comparable current densities, this option might be very attractive to consider.

There is no sufficient data to do the first assessment on the marginal cost for this paired production of lactobionic acid. It is very interesting to review the lactobionic acid and perform experiments of the different production methods as already reported.

## Conclusions and recommendations

This report provides a comprehensive overview of potential paired synthesis products and electrochemical conversion and is a very useful scouting report specifically focusing on the paired synthesis with an electrochemical catalytic CO<sub>2</sub> reduction.

This research project identified the possibility of producing some promising organic chemicals. These chemicals can be electro synthesized at rather low (ambient) temperatures and rather high current densities. The route to propylene oxide can contribute directly to the current aim of electrification of the chemical industry. All major technology needed is commercially available. The route to produce lactobionic acid from lactose has a low current density at present, but it might be a promising candidate after further investigation, as the feedstock, lactose, does not depend on oil and has the potential of being from a renewable source.

The business case of paired electrosynthesis is very attractive and the technology ready to be implemented; however, it is crucial to extend in the next phase on experiments of the different production methods, based on electrolytic oxidation, of lactobionic acid and propylene oxide. Experimental data is needed to have a better understanding of the impact on the reactor performance data and to be able to achieve a successfully paired synthesis.

It is highly recommended to start-up a follow-up project so that the outcome can be tested in combination with Coval Energy's technology.

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## Appendix A: Inorganic chemicals

Table 3: List of inorganic electrochemical processes[5]

Number	Product	Starting Material	Temperature	Type	Solubility	Decision
1	Aluminium	Al <sub>2</sub> O <sub>3</sub>	1000 C	Oxidation	Insoluble	
2	Chlorine/Caustic soda	NaCl	80-90 C	Redox	Ion	
3	Chloride/Sodium	HOCl	60-80 C	Redox	Ion	
4	Perchlorate	ClO <sub>3</sub> (-)	35-50 C	Oxidation	Ion	acceptable
5	Persulfate (S <sub>2</sub> O <sub>8</sub> ( <sup>2-</sup> ))	SO <sub>4</sub> ( <sup>2-</sup> )	cold	Oxidation	Ion	acceptable
6	Permanganate	NMnO <sub>4</sub> ( <sup>2-</sup> )	60 C	Oxidation	Ion	
7	Fluorine	F(-)	82 C	Oxidation	Gas	
8	Manganese dioxide	Mn( <sup>2+</sup> )	90-100 C	Oxidation	Insoluble	
9	Hydrogen peroxide	H <sub>2</sub> O	cold	Reduction	Soluble	
10	Hydrogen peroxide	H <sub>2</sub> S <sub>2</sub> O <sub>8</sub>		Oxidation	Soluble	acceptable
11	Ozone	O <sub>2</sub>	cold	Oxidation	Gas	acceptable
12	Dichromate	Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .x(H <sub>2</sub> O)		Oxidation	Ion	acceptable
13	Dinitrogen pentoxide	N <sub>2</sub> O <sub>4</sub>	cold	Oxidation	Insoluble (pure)	

## Appendix B: Organic Chemicals

Table 4: List of industrial organic electrosynthesis processes [5]

Number	Product	Starting Material	Company	Process operating status	Type	Molar mass	water solubility	Decision
1	Acetoin	Butanone	BASF	Commercial	N.F.	58.08	Soluble	
2	1-Acetonaphthalene	Naphthalene	BASF	Pilot	N.F.	200.24	Insoluble	
3	Acetylenedicarboxylic acid	1,4-Butynediol	BASF	Commercial	Reduction	114.06	Soluble	
4	Adipoin dimethyl acetal	Cyclohexanone	BASF	Commercial	N.F.	N.F.	Soluble	
5	Adiponitrile	Acrylonitrile	Monsanto (Solutia), BASF, Asahi Chemical	Commercial	Reduction	108.14	Soluble	
6	2-Aminobenzyl alcohol	Anthranilic acid	BASF	Pilot	Reduction	123.16	Partially Soluble	
7	4-Aminomethylpyridine	4-Cyanopyridine	Reilly Tar	Commercial	N.F.	108.14	Soluble	
8	Anthraquinone	Anthracene	L. B. Holliday, ECRC	Commercial	Oxidation	208.22	Insoluble	
9	Anthraquinone	Naphthalene, butadiene	Hydro Quebec	Pilot	Oxidation	208.22	Insoluble	
10	Arabinose	Gluconate	Electrosynthesis Co.	Pilot	Oxidation	150.13	Soluble	acceptable
11	Azobenzene	Nitrobenzene	Johnson Matthey Company	Commercial	Reduction	182.23	Insoluble	
12	Bleached montan wax	Raw montan wax	Clariant	Commercial	N.F.	N.A.	Insoluble	
13	1,2,3,4-Butanetetracarboxylic acid	Dimethyl maleate	Monsanto	Pilot	Reduction	234.16	Soluble	
14	p-t-Butylbenzaldehyde	p-t-Butyltoluene	BASF, Givaudan	Commercial	Oxidation	162.23	Partially Soluble	acceptable
15	Gluconate (Calcium gluconate)	Glucose	Sandoz, India	Commercial	Oxidation	196.16	Soluble	acceptable
16	Lactobionate (Calcium lactobionate)	Lactose	Sandoz, India	Commercial	Oxidation	754.65	Soluble	acceptable
17	S-Carbomethoxymethylcysteine	Cysteine + chloroacetic acid	Spain	Commercial	Reduction	N.F.	N.F.	
18	Ceftibuten	Cephalosporin C	Electrosynthesis Co., Schering Plough	Pilot	Reduction	410.42	Insoluble	
19	L-Cysteine	L-Cystine	Wacker Chemie AG	Commercial	Reduction	121.15	Soluble	
20	Diacetone-2-ketogulonic acid	Diacetone-L-sorbose	Hoffman-LaRoche	Commercial	Oxidation	N.F.	N.F.	

Number	Product	Starting Material	Company	Process operating status	Type	Molar mass	water solubility	Decision
21	Dialdehyde starch	Starch	CECRI	Commercial	Oxidation	N.A.	Soluble	
22	3,6-Dichloropicolinic acid	3,4,5,6-Tetrachloro-picolinic acid	Dow	Pilot	Reduction	192.00	Soluble	
23	1,4-Dihydronaphthalene	Naphthalene	Clariant	Commercial	Reduction	130.19	Insoluble	
24	1,2-Dihydrophthalic acid	<i>o</i> -Phthalic acid	BASF	Discontinued commercial	N.F.	166.14	N.F.	
25	2,5-Dimethoxy-2,5-dihydrofuran	Furan	BASF	Commercial	Oxidation	130.14	Insoluble (start)	
26	2,5-Dimethoxy-2,5-dihydrofuryl-1-ethanol	Furfuryl-1-ethanol	Otsuka	Commercial	N.F.	N.F.	N.F.	
27	Dimethylsebacate	Monomethyladipate	Asahi Chemical	Commercial	N.F.	230.30	Insoluble	
28	Ditolyliodonium salts (Ditolyliodonium)	<i>p</i> -Iodotoluene, toluene	Eastman Chemical, Electrosynthesis Co.	Pilot	Oxidation	176.12	Insoluble (start)	
29	Ethylene glycol	Formaldehyde	Electrosynthesis Co.	Pilot	Reduction	62.07	Soluble	
30	Gluconic acid	Glucose	Sandoz, India	Commercial	Oxidation	196.16	Soluble	acceptable
31	Glyoxylic acid	Oxalic acid	Rhone Poulenc, Steeley	Pilot	Reduction	74.04	Soluble	
32	Hexafluoropropyleneoxide	Hexafluoropropylene	Clariant	Commercial	N.F.	166.02	Insoluble (start)	
33	Hexahydrocarbazole	Tetrahydrocarbazole	L. B. Holliday, BASF	Discontinued commercial	Reduction	173.26	Insoluble (start)	
34	<i>m</i> -Hydroxybenzyl alcohol	<i>m</i> -Hydroxybenzoic acid	Otsuka	Commercial	Reduction	124.14	Partially Soluble	
35	Hydroxymethylbenzoic acid	Dimethyl terephthalate	Clariant	Pilot	Reduction	152.15	Partially Soluble	
36	<i>p</i> -Methoxybenzaldehyde	<i>p</i> -Methoxytoluene	BASF	Commercial	Oxidation	136.15	Partially Soluble	acceptable
37	2-Methylhydroindole	2-Methylindole	L. B. Holliday, BASF	Discontinued commercial	Reduction	162.19	N.F.	
38	Monochloroacetic acid	tri- and di-Chloroacetic acid	Clariant	Pilot	Reduction	94.50	Soluble	
39	Mucic acid (Galactaric acid)	Galacturonic acid	EDF	Commercial	Oxidation	210.14	Insoluble (cold)	
40	Nitrobenzene	<i>p</i> -Aminophenol	India, Monsanto	Pilot	Reduction	123.06	Partially Soluble	
41	5-Nitronaphthoquinone	1-Nitronaphthalene	Hydro Quebec	Pilot	Oxidation	148.01	Insoluble (start)	
42	Partially fluorinated hydrocarbons	Alkanes and alkenes	Phillips Petroleum	Pilot	Oxidation	N.A.	Insoluble (start)	
43	Perfluorinated hydrocarbons	Alkyl substrates	3M, Bayer, Clariant	Commercial	Oxidation	N.A.	Insoluble (start)	

Number	Product	Starting Material	Company	Process operating status	Type	Molar mass	water solubility	Decision
44	Phthalide + <i>t</i> -Butylbenzaldehyde acetal	Dimethyl phthalate + <i>t</i> -Butyltoluene	BASF	Commercial	Reduction	296.37	Partially Soluble	
45	Pinacol	Acetone	BASF, Diamond Shamrock	Pilot	Reduction	118.17	Soluble (not cold)	
46	Piperidine	Pyridine	Robinson Bros.	Discontinued commercial	Reduction	85.115	Soluble	
47	Polysilanes	Chlorosilanes	Osaka Gas	Commercial	Reduction	N.A.	Insoluble	
48	Propiolic acid	Propargyl alcohol	BASF	Pilot	Oxidation	70.05	Soluble	acceptable
49	Propylene oxide	Propylene	Kellog, Shell	Pilot	Oxidation	58.07	Insoluble (2 g/lit)	
50	Salicylic aldehyde	<i>o</i> -Hydroxybenzoic acid	India	Commercial	Oxidation	122.12	Insoluble (start)	
51	Sorbitol	Glucose	Hercules	Discontinued commercial	Reduction	182.17	Soluble	
52	Substituted benzaldehydes	Substituted toluenes	Hydro Quebec, W.R. Grace	Pilot	Oxidation	N.A.	Insoluble	
53	Succinic acid	Maleic acid	CERCI, India	Commercial	Reduction	118.09	Soluble	
54	Tetraalkyl lead	Alkyl halide	Nalco	Discontinued commercial	Reduction	N.A.	Insoluble	
55	3,4,5-Trimethoxybenzaldehyde	3,4,5-Trimethoxytoluene	Otsuka Chemical	Commercial	N.F.	196.20	Insoluble	
56	3,4,5-Trimethoxytolyl alcohol	3,4,5-Trimethoxytoluene	Otsuka Chemical	Commercial	N.F.	198.22	N.F.	
VC1	Erythritol	Starch/sugars	DFI	Pilot	Oxidation	122.12	Soluble	acceptable
VC2	Isoindoles	Phthalimides	CIBA	Commercial	Reduction	117.15	Insoluble (start)	
VC3	Cyclohexadienedicarboxylic acid	Phthalic acid	BASF	Commercial	N.F.	172.18	Soluble	
VC4	Xylitol	Starch/sugars	DFI	Pilot	Reduction	152.15	Soluble	