Supplementary Information (SI) for Green Chemistry.

Supporting Information: Setting Benchmarks for Ethylene and Propylene Oxidation via Electrochemical Routes: A Process Design and Technoeconomic Analysis Approach

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S1. Introductory and Background Information

S1.1 Detailed Descriptions of Reaction Mechanisms for the Reactions Modeled

Lum et al. investigated the oxidation of ethylene to EO and EG on a variety of Pd-based catalysts. They achieved an EG FE of ~60% with Pd dendritic nanostructures. They propose that the electrooxidation of ethylene to ethylene glycol proceeded through the successive transfer of two OH groups to ethylene, involving the intermediate $*C_2H_4OH$. Through bulk electrolysis and CV studies, they showed that increased *OH coverage promotes ethylene glycol formation and activates the catalyst. The EG FE was increased to 70% through doping the Pd dendritic nanostructures with Au. Density functional theory experiments suggest that the Au performs the transfer step of OH to $* C_2H_4OH$ easily and allows for the facile desorption of ethylene glycol, reducing further oxidation. Low EO FE (<3%) was observed for all materials tested.[1]

Ke et al. investigated three facets of Ag_3PO_4 ((100), (110), (111)) for electrochemical propylene oxidation and found that the (100) facet (corresponding to Ag_3PO_4 cubes) had the highest activity of the three. They used DFT calculations and ATR-FTIRS to prove that the electroepoxidation of propylene (Pr) over Ag_3PO_4 crystals undergoes an OH-correlated pathway rather than an O-correlated and dehydrogenation pathway. In the OH-correlated pathway, H_2O adsorbs and dissociates into *OH on Ag sites. This *OH reacts with Pr* to produce a bidentate PrOH* intermediate, which then transports to a PrO* intermediate through O-H bond dissociation of PrOH*. The PrO* is then transformed to PO* before desorption. The apparent activation energy barrier for the OH-correlated pathway was lower than for the O-correlated pathway. Density functional theory calculations and OH^- and propylene stripping experiments show that the (100) facet had the lowest propylene and OH* adsorption energies of the three Ag_3PO_4 facets, providing evidence as to why the (100) facet has the highest activity.[2]

Using DFT and ATR-FTIR, Winiwarter et al. thoroughly investigate the pathways of electrochemical propylene oxidation to allyl alcohol, acrolein, and acrylic acid, but only briefly comment on the oxidation of propylene to propylene glycol. They note that on Pd, propylene glycol is only produced significantly at potentials >1.0 V_{RHE}. They propose that at high potentials, lower coverage of propylene-derived species, evident through stripping experiments, can enable vinyl group coordination, allowing for oxidation of the double bond. They suggest product selectivity can be manipulated through surface coverage, as the coverage affects the propylene adsorbate geometry, which can lead to different reaction pathways. The formation of propylene oxide and propylene glycol can be promoted through the selective activation of the propylene vinyl group on weaker adsorption sites.[3]

Table S1. Detailed electrochemical ethylene and propylene epoxidation literature data.

System Name	Catalyst	Epoxidation FE (%)	Glycol FE (%)	Current Density (mA cm^{-2})	Electrolyte Composition	Potential	Cell	Major Products	Notes	Reference
E1	PdAu (Au 3.2at%) Dendritic Nanostructures/Glass Carbon	0.634	70	4.75	Ethylene saturated 0.1 M NaClO4	1.1 $V_{Ag/AgCl}$	3-compartment semi-batch	ethylene glycol, glycolaldehyde, acetaldehyde, ethylene oxide, formic acid	*FE Current density taken from Figure S33, taken at end of 100 h run	1
E2	PdO•H2O	-	42	3	Ethylene saturated 0.1 M NaClO4	1.1 $V_{Ag/AgCl}$	3-compartment semi-batch	ethylene glycol, glycolaldehyde, acetaldehyde, ethylene oxide	*FE Current density taken from Figure S21, taken at end of 2 h run	1
E3	Pd Nanoparticle	3	12	1	Ethylene saturated 0.1 M NaClO4	1.1 $V_{Ag/AgCl}$	3-compartment semi-batch	ethylene glycol	*FE Current density taken from Figure S21, taken at end of 2 h run	1
E4	Pd Powder	2	11	0.85	Ethylene saturated 0.1 M NaClO4	1.1 $V_{Ag/AgCl}$	3-compartment semi-batch	ethylene glycol, acetaldehyde, ethylene oxide	*FE Current density taken from Figure S21, taken at end of 2 h run	1
P1	Ag_3PO_4 (100) Cubes	19	-	2.05	0.1 M Phospahte Buffer Solution	2.2 V_{RHE}	3-compartment Semi-Batch	Propylene oxide, acetone, acetic acid	Current Density and FE taken from Figures 2a and b	2
P2	Ag_3PO_4 (110) Rhombic Dodecahedra	17	-	1.88	0.1 M Phospahte Buffer Solution	2.2 V_{RHE}	3-compartment Semi-Batch	Propylene oxide, acetone, acetic acid	Current Density and FE taken from Figures 2a and b	2
P3	Ag_3PO_4 (111) Tetrahedra	13	-	1.23	0.1 M Phospahte Buffer Solution	2.2 V_{RHE}	3-compartment Semi-Batch	Propylene oxide, acetone, acetic acid	Current Density and FE taken from Figures 2a and b	2
P4	Pd/Glassy Carbon	-	17	0.001	0.1 M $HClO_4$	1.1 V_{RHE}	H-cell	Propylene glycol, acrolein, allyl alcohol, acrylic acid, acetone, CO_2	Current Density and FE taken from Figures 2a and b	3

The three publications investigated in this work come from Lum et al., Ke et al., and Winiwarter et al. Lum et al. investigated the oxidation of ethylene to EO and EG on various Pd-based catalysts. They achieved an EG FE of ~60% with Pd dendritic nanostructures. The EG FE was increased to 70% through doping the Pd dendritic nanostructures with Au. Low EO FE (<3%) was observed for all materials tested.[1] Ke et al. investigated three facets of Ag_3PO_4 ((100), (110), (111)) for electrochemical propylene oxidation and found that the (100) facet (corresponding to Ag_3PO_4 cubes) had the highest activity of the three. They used DFT calculations and ATR-FTIRS to prove that the electroepoxidation of propylene (Pr) over Ag_3PO_4 crystals undergoes an OH-correlated pathway rather than an O-correlated and dehydrogenation pathway. Density functional theory calculations and OH^- and propylene stripping experiments show that the (100) facet had the lowest propylene and OH* adsorption energies of the three Ag_3PO_4 facets, proving why the (100) facet has the highest activity.[2] Using DFT and ATR-FTIR, Winiwarter et al. thoroughly investigate the pathways of electrochemical propylene oxidation to allyl alcohol, acrolein, and acrylic acid, but only briefly comment on the oxidation of propylene to propylene glycol. They note that propylene glycol is only produced significantly on Pd at potentials $>1.0\ V_{RHE}$.[3]

S1.2 Ethylene and Propylene Electrooxidation Reactions

Ethylene Electrooxidation Reactions

EO: $C_2H_4 + H_2O \rightarrow C_2H_4O + 2H^+ + 2e^-$

EG: $C_2H_4 + 2H_2O \rightarrow (CH_2OH)_2 + 2H^+ + 2e^-$

Glycolaldehyde: $C_2H_4 + 2H_2O \rightarrow C_2H_4O_2 + 4H^+ + 4e^-$

Acetaldehyde: $C_2H_4 + H_2O \rightarrow CH_3CHO + 2H^+ + 2e^-$

Formic Acid: $C_2H_4 + 4H_2O \rightarrow HCOOH + CO_2 + 6H^+ + 6e^-$

Propylene Electrooxidation Reactions

PO: $C_3H_6 + H_2O \rightarrow C_3H_6O + 2H^+ + 2e^-$

PG: $C_3H_6 + 2H_2O \rightarrow C_3H_8O_2 + 2H^+ + 2e^-$

Acetone: $C_3H_6 + H_2O \rightarrow (CH_3)_2CO + 2H^+ + 2e^-$

Acetic Acid: $C_3H_6 + 4H_2O \rightarrow CH_3COOH + CO_2 + 10H^+ + 10e^-$

Acrolein: $C_3H_6 + H_2O \rightarrow C_3H_4O + 4H^+ + 4e^-$

Allyl Alcohol: $C_3H_6 + H_2O \rightarrow C_3H_6O + 2H^+ + 2e^-$

Acrylic Acid: $C_3H_6 + 2H_2O \rightarrow C_3H_4O_2 + 6H^+ + 6e^-$

CO_2: $C_3H_6 + 6H_2O \rightarrow 3CO_2 + 18H^+ + 18e^-$

S1.3 U.S. Ethylene, EO, and EG Production

Table S2. U.S. Ethylene, EO, and EG producers and stated production capacities.

State	Facility Name	Company Name	County	Ethylene tonnes per year	EO tonnes per year	EG tonnes per year	References
TX	Port Arthur (BASF)	BASF/Total	Jefferson	892,857	N/A	N/A	4
TX	Port Arthur (Baystar)	Bayport Polymers, LLC	Jefferson	892,857	N/A	N/A	5 6
TX	Cedar Bayou	Chevron Phillips Chemical	Harris	1,339,286	N/A	N/A	7 8
TX	Port Arthur (CP Chem)	Chevron Phillips Chemical	Jefferson	763,393	N/A	N/A	9 10
TX	Sweeny	Chevron Phillips Chemical	Brazoria	597,132	N/A	N/A	11 12
TX	Freeport	Dow Chemical Co.	Brazoria	3,250,000	N/A	N/A	13
LA	Plaquemine	Dow Chemical Co.	Iberville	1,321,429	241,071	92,857	14
LA	Taft	Dow Chemical Co.	Saint Charles	1,000,000	687,500	625,000	15 16
TX	Orange	Dow Chemical Co.	Orange	882,000	N/A	N/A	17
TX	Longview	Eastman Chemical Co.	Gregg	892,857	93,750	81,018	18 19 16
TX	Portland	Exxon/SABIC	San Patricio	787,500	N/A	982,143	20 21
LA	Baton Rogue	ExxonMobil Chemical Co.	East Baton Rouge	571,429	N/A	N/A	22
TX	Baytown (ExxonMobil)	ExxonMobil Chemical Co.	Harris	1,607,143	N/A	N/A	23
TX	Beaumont	ExxonMobil Chemical Co.	Jefferson	919,643	N/A	N/A	24

State	Facility Name	Company Name	County	Ethylene tonnes per year	EO tonnes per year	EG tonnes per year	References
TX	Port Arthur (Motiva)	Motiva	Jefferson	3,250,000	N/A	N/A	25
TX	Point Comfort	Formosa Plastics Corp. USA	Calhoun	803,571	223,214	1,066,071	26
LA	Carlyss	Indorama Ventures Olefins, LLC	Calcasieu	330,357	N/A	N/A	27
TX	Port Neches	Indorama Ventures Olefins, LLC	Jefferson	428,571	1,160,714	860,714	28
TX	Chocolate Bayou (INEOS)	INEOS Olefins and Polymers	Brazoria	1,616,071	464,286	N/A	29
TX	Channelview	LyondellBasell Industries	Harris	1,660,714	N/A	N/A	30 31
TX	Chocolate Bayou (Lyondell Basell)	LyondellBasell Industries	Brazoria	486,607	N/A	N/A	32
IA	Clinton	LyondellBasell Industries	Clinton	535,714	N/A	N/A	33
TX	Corpus Christi	LyondellBasell Industries	Nueces	1,116,071	N/A	N/A	34
TX	La Porte	LyondellBasell Industries	Harris	1,026,786	N/A	N/A	35
IL	Morris	LyondellBasell Industries	Grundy	1,026,786	N/A	N/A	36
LA	Geismar	Nova Chemicals	Ascension	870,536	N/A	N/A	37
TX	Ingleside	Occidental Chemical/Mexichem	San Patricio	491,071	N/A	N/A	38
LA	Lake Charles (Sasol)	Sasol	Calcasieu	1,339,286	267,857	223,214	39 40 41
TX	Deer Park	Shell Chemicals Ltd.	Harris	750,000	N/A	N/A	42
LA	Norco	Shell Chemicals Ltd.	Saint Charles	1,486,607	N/A	N/A	43
LA	Plaquemine	Shinetsu	Plaquemine	446,429	N/A	N/A	44

State	Facility Name	Company Name	County	Ethylene tonnes per year	EO tonnes per year	EG tonnes per year	References
KY	Calvert City	Westlake Petrochemicals Corp.	Marshall	325,893	N/A	N/A	45
LA	Sulphur	Westlake Petrochemicals Corp.	Calcasieu	669,643	N/A	N/A	46
LA	Lake Charles (Westlake)	Westlake/Lotte	Calcasieu	669,643	N/A	N/A	45
PA	Franklin Monaca	Shell Chemicals Ltd.	Beaver	1,339,286	N/A	N/A	47
LA	Sunshine Project	Formosa Plastics Corp. USA	St. James	2,142,857	Produced but no capacity stated	1,428,571	48
OH	GC America	PTT Global Chemical/Marubeni/Daelim Chemical	Belmont	1,339,286	N/A	N/A	47
TX	Orange	Chevron Phillips Chemical Co. LP	Orange	1,339,286	N/A	N/A	47
TX	Clear Lake	Indorama Ventures (Oxide and Glycols)	Harris	N/A	388,393	319,643	49
TX	Chocolate Bayou	Indorama Ventures (Oxide and Glycols)	Brazoria	N/A	Utilize EO to create various products	N/A	50
TX	Dayton	Indorama Ventures (Oxide and Glycols)	Liberty	N/A	Utilize EO to create various products	N/A	51
LA	Geismar	BASF	Ascension	N/A	196,429	Unable to determine	52
TX	Seadrift	Dow Chemical Co.	Calhoun	N/A	383,929	232,143	19
TX	Bayport Polymers	Lyondell Basell	Harris	N/A	321,429	53,571	19 53
LA	Geismar	Shell Chemicals Ltd.	Ascension	N/A	410,714	370,536	54
TX	Oyster Creek	MEGlobal	Brazoria	N/A	N/A	669,643	55

State	Facility Name	Company Name	County	Ethylene tonnes per year	EO tonnes per year	EG tonnes per year	References
LA	Lotte Chemical Louisiana	Lotte Chemical	Calcasieu	N/A	N/A	625,000	56
Total				42,679,275	4,839,286	7,630,125	
Average				1,123,139	403,274	579,790	
Median				892,857	352,679	625,000	

S1.4 U.S. Propylene, PO, and PG Production

Table S3. U.S. Propylene, PO, and PG producers and stated production capacities

Facility State	Facility Name	Company Name	County	Propylene tonnes per year	PO tonnes per year	PG tonnes per year	References
TX	Port Arthur (BASF)	BASF/Total	Jefferson	494,643	N/A	N/A	4
TX	Port Arthur (Baystar)	Bayport Polymers, LLC	Jefferson	558,036	N/A	N/A	5 6
TX	Cedar Bayou	Chevron Phillips Chemical	Harris	401,786	N/A	N/A	7 8
TX	Port Arthur (CP Chem)	Chevron Phillips Chemical	Jefferson	405,357	N/A	N/A	9 10
TX	Sweeny	Chevron Phillips Chemical	Brazoria	491,071	N/A	N/A	11 12
TX	Freeport	Dow Chemical Co.	Brazoria	1,133,929	647,321	N/A	13
LA	Plaquemine	Dow Chemical Co.	Iberville	321,429	294,643	294,643	57 58
LA	Taft	Dow Chemical Co.	Saint Charles	266,964	N/A	N/A	59
LA	Baton Rogue	ExxonMobil Chemical Co.	East Baton Rouge	866,071	N/A	N/A	22
TX	Baytown (ExxonMobil)	ExxonMobil Chemical Co.	Harris	857,143	N/A	N/A	23
TX	Port Arthur (Motiva)	Motiva	Jefferson	303,571	N/A	N/A	25
TX	Point Comfort	Formosa Plastics Corp. USA	Calhoun	587,500	N/A	N/A	26 60
LA	Carlyss	Indorama Ventures Olefins, LLC	Calcasieu	26,786	N/A	N/A	27
TX	Port Neches	Indorama Ventures Olefins, LLC	Jefferson	35,714	468,750	129,464	28
TX	Chocolate Bayou (INEOS)	INEOS Olefins and Polymers	Brazoria	357,143	N/A	N/A	29
TX	Channelview	LyondellBasell Industries	Harris	1,375,000	446,429	N/A	30 31
TX	Chocolate Bayou	LyondellBasell Industries	Brazoria	293,750	N/A-	N/A	32

Facility State	Facility Name	Company Name	County	Propylene tonnes per year	PO tonnes per year	PG tonnes per year	References
TX	Corpus Christi	LyondellBasell Industries	Nueces	254,464	N/A	N/A	34
TX	La Porte	LyondellBasell Industries	Harris	283,036	N/A	N/A	35
LA	Geismar	Nova Chemicals	Ascension	50,893	N/A	N/A	37
TX	Deer Park	Shell Chemicals Ltd.	Harris	446,429	N/A	N/A	42
LA	Norco	Shell Chemicals Ltd.	Saint Charles	642,857	N/A	N/A	43
LA	Sunshine Project	Formosa Plastics Corp. USA	St. James	535,714	N/A	N/A	48
TX	Tyler Refinery	Delek	Smith	81,250	N/A	N/A	59
AR	El Dorado Refinery	Delek	Union	35,714	N/A	N/A	61
LA	Garyville Refinery	Marathon Petroleum	St. John the Baptist	324,107	N/A	N/A	59
LA	PBF Chalmette Refinery	PDF Energy	St. Bernard	121,429	N/A	N/A	59
LA	Alliance Refinery	Phillips 66	Plaquemine	196,429	N/A	N/A	59
LA	Placid Refinery	Placid Refining Company	West Baton Rouge	20,536	N/A	N/A	59
LA	St. Charles Refinery	Valero	St. Charles	80,357	N/A	N/A	59
TX	No Name	INVISTA	Harris	587,500	N/A	N/A	62 63
TX	No Name	Enterprise	Chambers	4,910,714	N/A	N/A	64 63
TX	No Name	PetroLogistics	Undefined Location currently	446,429	N/A	N/A	65
TX	Bayport Polymers	Lyondell Basell	Harris	N/A	535,714	Capacity not stated	66
Total				17,793,750	2,392,857	424,107	
Average				539,205	478,571	212,054	
Median				357,143	468,750	212,054	

S1.5 Calculations for Single-Pass Conversion and Stoichiometric Reaction from Reported Literature Values for Ethylene Systems Example

Lum et al. provided details on the observed cell potentials, current density, electrode area, experimental run times, reactor volumes, and Faradaic efficiencies (FE) for each product. First, the total charge passed, Q, is calculated from the current density, J, electrode area, A, and experimental run time, t,

$$Q = J \cdot A \cdot t \qquad \textbf{Eq. 1}$$

The moles of each product formed, N_i, was calculated from the electron requirement, e_i, shown in Section S1.2 the reported Faradaic efficiencies for each product, FE_i, and Faraday's constant, F.

$$N_i = \frac{FE_i \cdot Q}{e_i \cdot F} \qquad \textbf{Eq. 2}$$

The conversion percentage of ethylene, $Conv_{eth}$, is then determined by summing N_i and the carbon count of each product, $Carbon_i$, over the total moles present of ethylene, $N_{eth,t=0}$, at the start of the reaction,

$$Conv_{eth} = \frac{\sum_{i}^{n} N_i \cdot Carbon_i}{N_{eth,t=0} \cdot Carbon_{eth}} \qquad \textbf{Eq. 3}$$

As the studied literature was primarily done in a batch process, it is assumed that the same conversion would occur per single pass in a gas diffusion electrode assembly in a flow by operation. To model the reaction in SuperPro Designer in a stoichiometric reactor, the number of moles of each product formed per mole of ethylene converted per single pass, n_i, is determined.

$$n_i = \frac{N_i \cdot Carbon_i}{Conv_{eth} \cdot N_{eth,t=0} \cdot Carbon_{eth}} \qquad \textbf{Eq. 4}$$

S1.6 Detailed Singe Pass Conversion and Carbon Selectivity by System

Table S4. Reported reactant single pass conversion percentages and carbon selectivities for studied ethylene electrooxidation literature systems.

System Name	Single Pass Conversion %	EO	EG	Glycolaldehyde	Acetaldehyde	Formic Acid	Source
System E1	0.0095%	0.8%	86.4%	7.4%	2.6%	5.6%	1
System E2	0.0026%	5.7%	79.2%	6.6%	8.5%	N/A	1
System E3	0.0002%	N/A	100%	N/A	N/A	N/A	1
System E4	0.0002%	12.1%	66.7%	N/A	21.2%	N/A	1

Table S5. Reported reactant single pass conversion percentages and carbon selectivities for studied propylene electrooxidation literature systems.

System Name	Single Pass Conversion %	PO	PG	Acetone	Acetic Acid	Acrolein	Allyl Alcohol	Acrylic Acid	CO_2	Source
System P1	11.4%	80.8%	N/A	14.9%	6.5%	N/A	N/A	N/A	N/A	2
System P2	14.1%	79.5%	N/A	16.6%	5.9%	N/A	N/A	N/A	N/A	2
System P3	12.4%	73.2%	N/A	22.0%	7.3%	N/A	N/A	N/A	N/A	2
System P4	0.0014%	N/A	33.6%	49.4%	N/A	6.9%	3.9%	0.6%	16.5%	3

S2. Saturated Aqueous Electrochemical Process Models

S2.1 Saturated Aqueous Electrochemical Ethylene Process Model

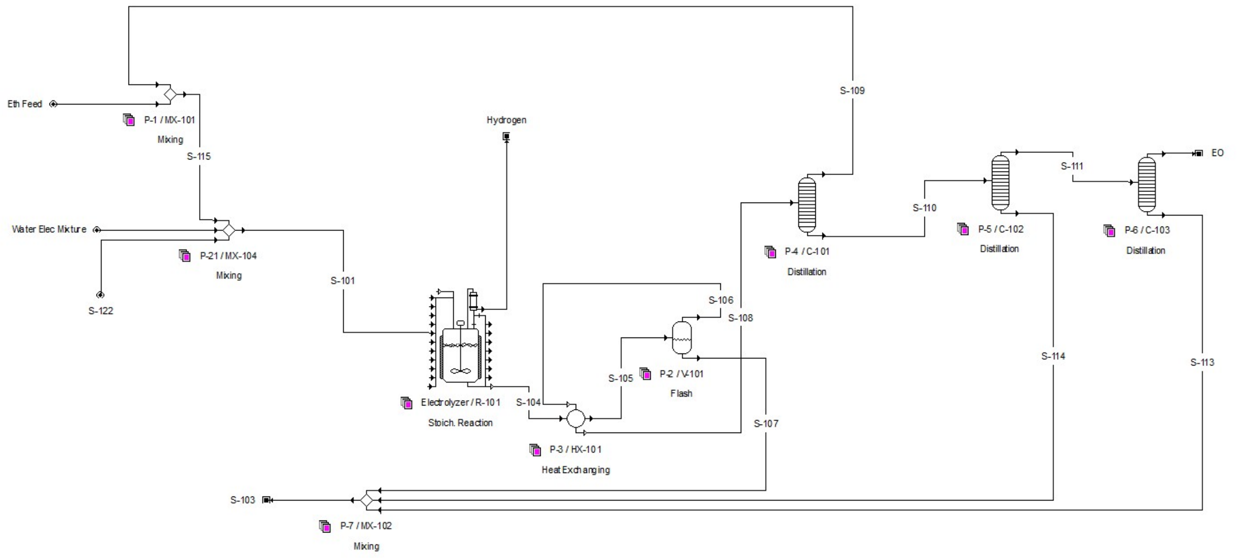

Figure S1. Aqueous electrochemical ethylene oxidation process model flow diagram in SuperPro Designer.

The saturated aqueous ethylene electrooxidation process model assumes a 453 ktonnes per year ethylene feed rate at standard temperature and pressure (STP). In this model, a premixed water and electrolyte mixture at STP with a 0.1 M $NaClO_4$ concentration at varied total flow rates as shown in Table S6 is mixed with a previously combined fresh ethylene stream and recycled ethylene stream. The water electrolyte mixture was varied to ensure the ethylene is saturated in the electrolyte solution where ethylene has a solubility of 131 mg/L at STP. This stream is then fed to a stoichiometric reactor assuming a 100% carbon selectivity for EO and varied single pass conversion rates as shown in Table S4. A stoichiometric volume of hydrogen is assumed to be produced in this reaction to mimic that of an electrolyzer that is assumed to be separated within the reactor. The reaction is carried out at STP to mimic the conditions of an electrochemical process. As the unreacted ethylene and EO would be solubilized in this reactor system, both gaseous products must be separated from the liquid stream. This liquid stream from the reactor is passed through a countercurrent shell and tube heat exchanger with an assumed heat transfer coefficient of 1,500 W/m^2-K to elevate the temperature. The liquid stream is then flashed in a separator set to maximize the recovery of EO in the vapor stream. The liquid stream is discarded, and the vapor stream passed back to the heat exchanger and is then passed to an atmospheric distillation column to recover 99.99% purity ethylene as the distillate to recycle back to the reactor. The liquid stream then passes through two distillation columns to recover the EO. The liquid streams are not shown to be recovered in the model; however, no cost is assumed for the $NaClO_4$ as the electrolyte could be reutilized as a non-consumable material in the reaction process.

Table S6. Electrolyte solution flow rates required to solubilize ethylene at STP in the aqueous ethylene electrooxidation model at varied ethylene single pass conversion percentages.

Ethylene Single Pass Conversion %	**Electrolyte Solution Flow Rate (kL/s)**
10%	1,100
20%	540
30%	360
40%	270
50%	210
60%	175
70%	150
80%	130
90%	120

S2.2 Saturated Aqueous Electrochemical Propylene Process Model

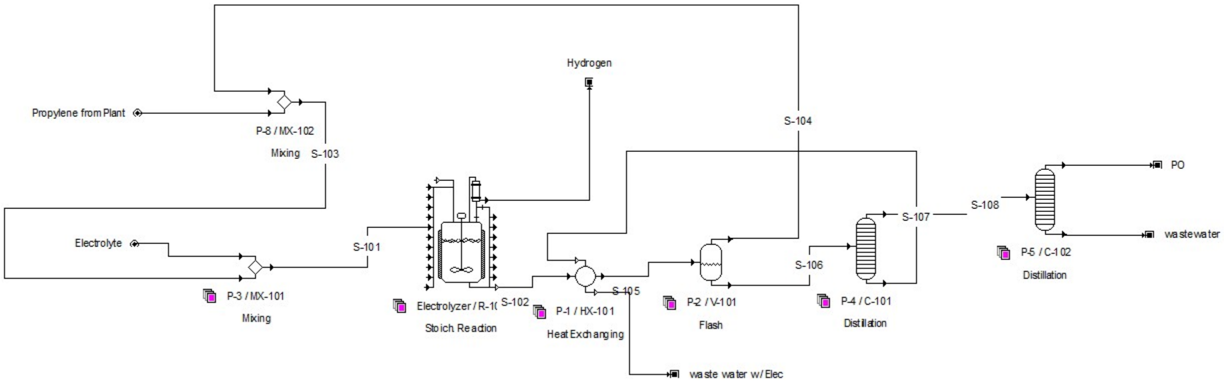

Figure S2. Aqueous propylene electrooxidation process model flow diagram.

The saturated aqueous electrochemical propylene electrooxidation model assumes a 181 ktonnes per year propylene feed rate at STP. In this model, a premixed water and electrolyte mixture at STP with a 0.1 M phosphate buffer concentration at varied total flow rates (Table S7) is mixed with a previously combined fresh propylene stream and recycled propylene stream. The water electrolyte mixture was varied to ensure the propylene is saturated in the electrolyte solution where propylene has a solubility of 200 mg/L at STP. This stream is then fed to a stoichiometric reactor assuming a 100% carbon selectivity for PO and varied single pass conversion rates as shown in Table S5. A stoichiometric volume of hydrogen is assumed to be produced in this reaction to mimic that of an electrolyzer that is assumed to be separated within the reactor. The reaction is carried out at STP to mimic the conditions of an electrochemical process. As the unreacted propylene would be solubilized in this reactor system, and PO is a liquid at these conditions, both products must be separated. This liquid stream from the reactor is passed through a countercurrent shell and tube heat exchanger with an assumed heat transfer coefficient of 1,500 W/m^2-K to elevate the temperature. The liquid stream is then flashed in a separator set to maximize the recovery of propylene in the vapor stream that is then recycled back to the reactor. The liquid stream is then passed to an atmospheric distillation column to recover 99.99% of the PO. The liquid stream is used to preheat the post reaction liquid stream. A secondary distillation column is utilized to further purify the PO stream. The liquid streams are not shown to be recovered in the model; however, no cost is assumed for the phosphate buffer as the electrolyte could be reutilized as a non-consumable material in the reaction process.

Table S7. Electrolyte solution flow rates required to solubilize propylene at STP in the saturated aqueous propylene electrooxidation model at varied propylene single pass conversion percentages.

Propylene Single Pass Conversion %	**Electrolyte Solution Flow Rate (kL/s)**
10%	280
20%	145
30%	95
40%	70
50%	56
60%	47
70%	40
80%	35
90%	31

S3. Gaseous Electrochemical Ethylene Epoxidation Process Models and Additional Results Summaries

S3.1 System E1 Electrochemical Ethylene Epoxidation Process Model

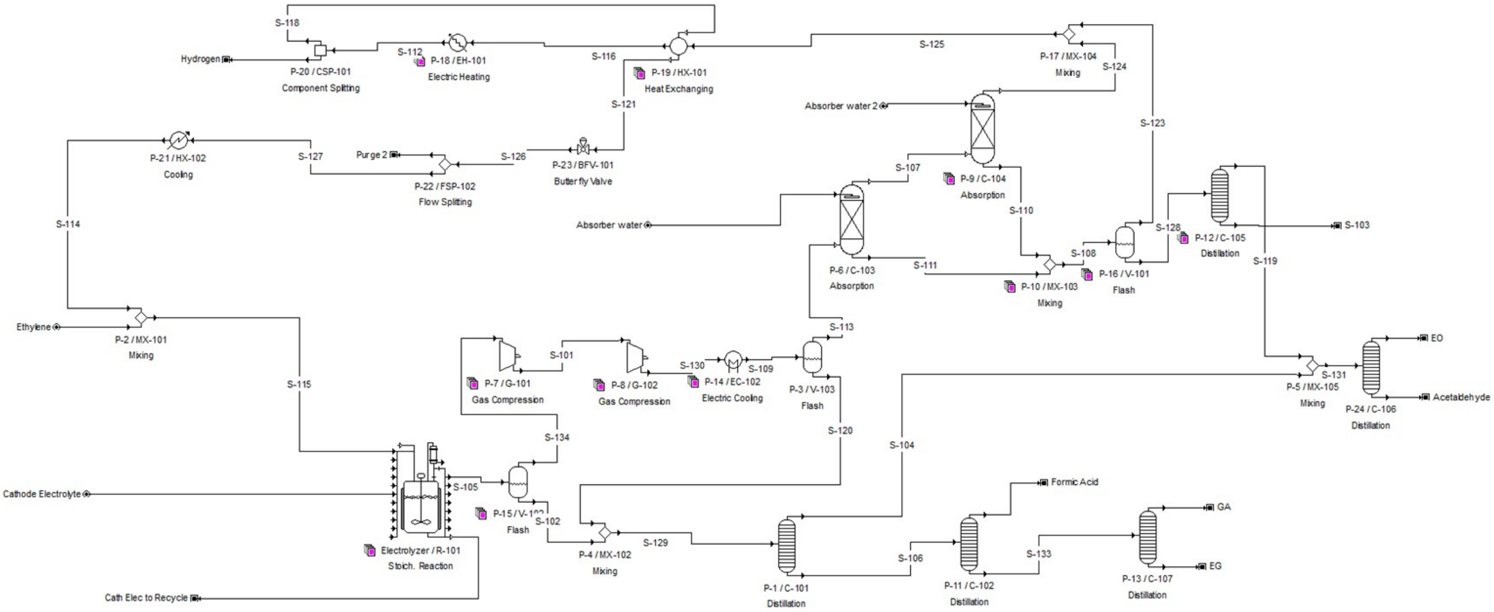

Figure S3. Gaseous ethylene electrooxidation process model flow diagram for literature System E1.

The gaseous ethylene electrooxidation process model for System E1 assumes a 453k tonnes per year ethylene feed rate at STP. In this model, a premixed water and electrolyte mixture at STP with a 0.1 M $NaClO_4$ concentration is mixed with a previously combined fresh ethylene stream and recycled ethylene stream. This stream is then fed to a stoichiometric reactor assuming carbon selectivities as stated in Table S4 and varied single pass conversion rates as shown in Table S8. A stoichiometric volume of hydrogen is assumed to be produced in this reaction to mimic that of an electrolyzer. The reaction is carried out at STP to mimic the conditions of an electrochemical process. To model the reactor like an electrolyzer, the reactor is set to split the streams with all cathode side products, unreacted ethylene, hydrogen, and oxygen leaving the top of the reactor and the water and electrolyte (anode side) leaving the bottom of the reactor. The anode side

stream recycle is not shown in the figure; however, the cost for this stream is set to zero to account for the potential to recycle the stream.

The cathode side components leaving the reactor for System E1 are ethylene, EO, acetaldehyde, EG, glycolaldehyde, formic acid, H_2, and O_2. As SuperPro Designer does not have a built in electrolyzer unit operation, we determined energy requirements, maintenance costs, and capital cost of the reactor with an external model based on the DOE H2A model.[67]

The cathode side stream from the reactor is sent to a flash vessel at 25 °C and 1 bar to recover as much of the liquid stream as possible modeled by Henry's Law in the process design software. The remaining gaseous products from the reactor are compressed via a two-stage compressor system (80% efficiency) with interstage electric cooling to 30 bar. The stream then passes to another separator to remove as much of the liquids as possible to be sent to the liquid recovery train. The compressed gas stream then passes through a first absorption column fed with water at 25 °C at 30 bar at varied required rates shown in Table S8. At these conditions, 53.15% of the acetaldehyde, 53.15% of the EO, 0.4385% of the ethylene, and 0.02% of the hydrogen is assumed to be absorbed [68]. The unabsorbed gases then pass through a second absorption column with the same assumed absorption percentages to try and recover as much of the products as possible. The bottoms streams from both absorbers are combined and heated to 50 °C where the ethylene and H_2 are released and sent to a recycle train. The liquid stream from the flash vessel passes through a distillation column designed to recover 99.99% of both the acetaldehyde and EO in the distillate with the bottoms containing water. The distillate stream passes through a second distillation column designed to produce >90% by mass purity of EO with acetaldehyde as a bottoms stream.

The liquid stream is then passed to an atmospheric distillation column designed to recover the EO and acetaldehyde from the distillate that is then combined with the distillation from the gas side of the process to recover each product individually. The liquid stream now containing formic acid, glycolaldehyde, and EG is passed to a second atmospheric distillation column set to recover 99.99% of the formic acid in the distillate. The bottoms stream of the second atmospheric distillation column containing primarily EG and glycolaldehyde are then passed to a third distillation column to separate the glycolaldehyde as the distillate and EG as the bottoms stream.

The recycle train of the system begins with the mixing of the unabsorbed gases from the absorber train that contains ethylene, unabsorbed EO, unabsorbed acetaldehyde, H_2, and O_2. The stream passes through a countercurrent heat exchanger followed by an electric heater are used to elevate the temperature to 200 °C. The heated stream is then split by a component splitter set to mimic a hydrogen separating membrane due to the lack of such a unit operation in SuperPro designer. The component splitter is assumed to recover 99% of the hydrogen as reported by available products from Air Liquide [69]. The remaining gas stream is then passed to the shell side of the countercurrent heat exchanger before passing through a butterfly valve to lower the pressure back to just over 1 atm. The stream then passes through a flow splitter used to mimic a purge system. The percentage of the stream that is purged is varied as shown in Table S8 to ensure that the ethylene stream fed to the reactor maintains an ethylene purity of >98% by mass. The remaining gas stream in the recycle loop is then cooled via an electric cooler to 25 °C before combining with the pure ethylene feed to reenter the system.

Table S8. Absorber water requirements and purge percentage requirements for the process model for System E1. Absorber water volumes are the minimum required flow rates to operate the column. Purge percentages are set to maintain a 98% purity of ethylene being fed to the reactor.

Ethylene Single Pass Conversion %	Absorber 1 Water Requirement (kmol/h)	Absorber 2 Water Requirement (kmol/h)	Purge Percentage
0.01%	29,000	29,000	50%
10%	59,400	59,100	20%
20%	40,300	40,200	33%
30%	34,600	34,500	43.0%
40%	32,700	32,700	50.0%
50%	32,000	31,900	56.0%
60%	32,200	32,100	60.0%
70%	32,600	32,500	64%
80%	34,300	34,200	67%
90%	34,300	34,200	71%

S3.2 System E2 Electrochemical Ethylene Epoxidation Process Model

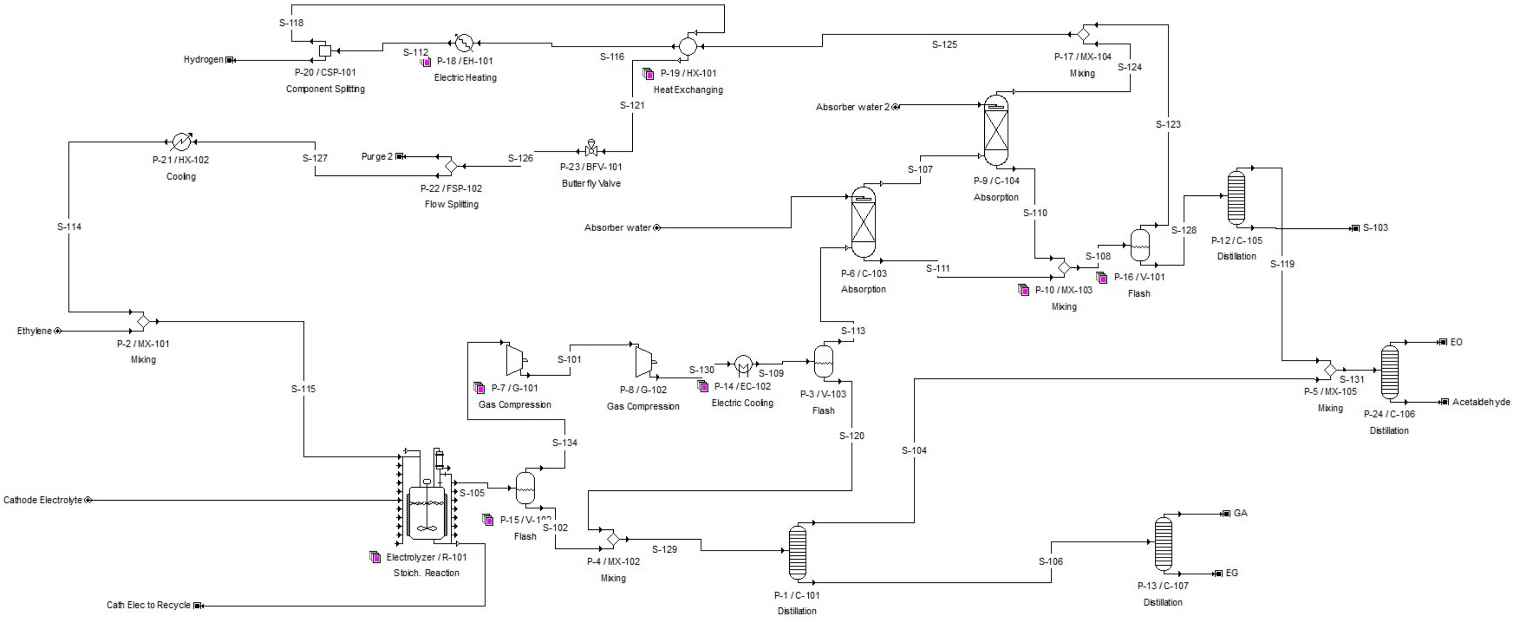

Figure S4. Gaseous ethylene electrooxidation process model flow diagram for literature System E2.

The gaseous ethylene electrooxidation process model for System E2 assumes a 453 ktonnes per year ethylene feed rate at STP. In this model, a premixed water and electrolyte mixture at STP with a 0.1 M $NaClO_4$ concentration is mixed with a previously combined fresh ethylene stream and recycled ethylene stream. This stream is then fed to a stoichiometric reactor assuming carbon selectivities as stated in Table S4 and varied single pass conversion rates as shown in Table S9. A stoichiometric volume of hydrogen is assumed to be produced in this reaction to mimic that of an electrolyzer. The reaction is carried out at STP to mimic the conditions of an electrochemical process. To model the reactor like an electrolyzer, the reactor is set to split the streams with all cathode side products, unreacted ethylene, hydrogen, and oxygen leaving the top of the reactor and the water and electrolyte (anode side) leaving the bottom of the reactor. The anode side

stream recycle is not shown in the figure; however, the cost for this stream is set to zero to account for the potential to recycle the stream.

The cathode side components leaving the reactor for System E2 are ethylene, EO, acetaldehyde, EG, glycolaldehyde, H_2, and O_2. As SuperPro Designer does not have a built in electrolyzer unit operation, we determined energy requirements, maintenance costs, and capital cost of the reactor with an external model based on the DOE H2A model.[67]

The cathode side stream from the reactor is sent to a flash vessel at 25 °C and 1 bar to recover as much of the liquid stream as possible modeled by Henry's Law in the process design software. The remaining gaseous products from the reactor are compressed via a two-stage compressor system (80% efficiency) with interstage electric cooling to 30 bar. The stream then passes to another separator to remove as much of the liquids as possible to be sent to the liquid recovery train. The compressed gas stream then passes through a first absorption column fed with water at 25 °C at 30 bar at varied required rates shown in Table S9. At these conditions, 53.15% of the acetaldehyde, 53.15% of the EO, 0.4385% of the ethylene, and 0.02% of the hydrogen is assumed to be absorbed [68]. The unabsorbed gases then pass through a second absorption column with the same assumed absorption percentages to try and recover as much of the products as possible. The bottoms streams from both absorbers are combined and heated to 50 °C where the ethylene and H_2 are released and sent to a recycle train. The liquid stream from the flash vessel passes through a distillation column designed to recover 99.99% of both the acetaldehyde and EO in the distillate with the bottoms containing water. The distillate stream passes through a second distillation column designed to produce >90% by mass purity of EO with acetaldehyde as a bottoms stream.

The liquid stream is then passed to an atmospheric distillation column designed to recover the EO and acetaldehyde from the distillate that is then combined with the distillation from the gas side of the process to recover each product individually. The liquid stream now containing glycolaldehyde and EG is passed to a second atmospheric distillation column to separate the glycolaldehyde as the distillate and EG as the bottoms stream.

The recycle train of the system begins with the mixing of the unabsorbed gases from the absorber train that contains ethylene, unabsorbed EO, unabsorbed acetaldehyde, H_2, and O_2. The stream passes through a countercurrent heat exchanger followed by an electric heater are used to elevate the temperature to 200 °C. The heated stream is then split by a component splitter set to mimic a hydrogen separating membrane due to the lack of such a unit operation in SuperPro designer. The component splitter is assumed to recover 99% of the hydrogen as reported by available products from Air Liquide [69]. The remaining gas stream is then passed to the shell side of the countercurrent heat exchanger before passing through a butterfly valve to lower the pressure back to just over 1 atm. The stream then passes through a flow splitter used to mimic a purge system. The percentage of the stream that is purged is varied as shown in Table S9 to ensure that the ethylene stream fed to the reactor maintains an ethylene purity of >98% by mass. The remaining gas stream in the recycle loop is then cooled via an electric cooler to 25 °C before combining with the pure ethylene feed to reenter the system.

Table S9. Absorber water requirements and purge percentage requirements for the process model for System E2. Absorber water volumes are the minimum required flow rates to operate the column. Purge percentages are set to maintain a 98% purity of ethylene being fed to the reactor.

Ethylene Single Pass Conversion %	**Absorber 1 Water Requirement (kmol/h)**	**Absorber 2 Water Requirement (kmol/h)**	**Purge Percentage**
0.01%	35,800	35,600	40%
10%	24,400	24,200	71.2%
20%	25,000	24,700	83.2%
30%	27,400	27,100	88.2%
40%	30,300	30,000	91.0%
50%	33,300	33,000	92.6%
60%	36,500	36,100	93.7%
70%	39,700	39,300	94.6%
80%	43,000	42,500	95.2%
90%	46,300	45,700	95.7%

S3.3 System E3 Electrochemical Ethylene Epoxidation Process Model

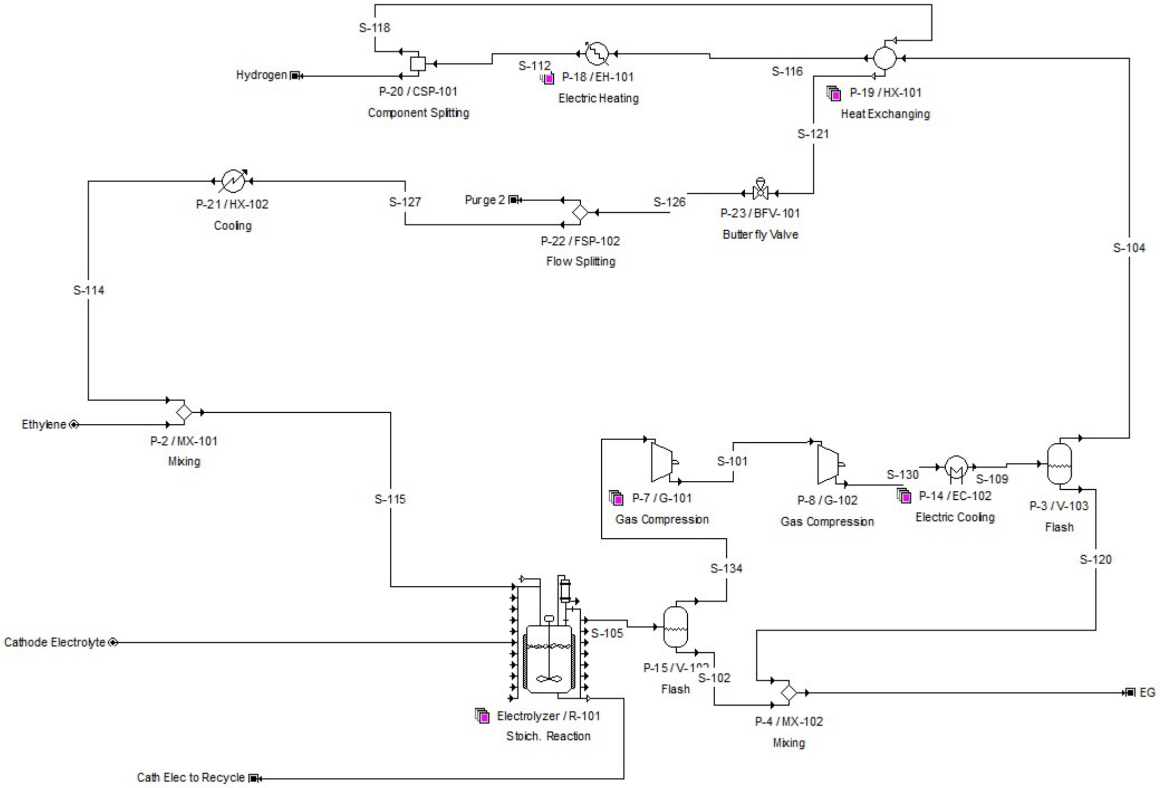

Figure S5. Gaseous ethylene electrooxidation process model flow diagram for literature System E3.

The gaseous ethylene electrooxidation process model for System E3 assumes a 453 ktonnes per year ethylene feed rate at STP. In this model, a premixed water and electrolyte mixture at STP with a 0.1 M $NaClO_4$ concentration is mixed with a previously combined fresh ethylene stream and recycled ethylene stream. This stream is then fed to a stoichiometric reactor assuming carbon selectivities as stated in Table S4 and varied single pass conversion rates as shown in Table S10. A stoichiometric volume of hydrogen is assumed to be produced in this reaction to mimic that of an electrolyzer. The reaction is carried out at STP to mimic the conditions of an electrochemical process. To model the reactor like an electrolyzer, the reactor is set to split the streams with all cathode side products, unreacted ethylene, hydrogen, and oxygen leaving the top of the reactor and the water and electrolyte (anode side) leaving the bottom of the reactor. The anode side stream recycle is not shown in the figure; however, the cost for this stream is set to zero to account for the potential to recycle the stream.

The cathode side components leaving the reactor for System E3 are ethylene, EG, H_2, and O_2. As SuperPro Designer does not have a built in electrolyzer unit operation, we determined energy requirements, maintenance costs, and capital cost of the reactor with an external model based on the DOE H2A model.[67]

The cathode side stream from the reactor is sent to a flash vessel at 25 °C and 1 bar to recover as much of the liquid stream as possible modeled by Henry's Law in the process design software. The remaining gaseous products from the reactor are compressed via a two-stage compressor system (80% efficiency) with interstage electric cooling to 30 bar. The stream then passes to another separator to remove as much of the liquids as possible to be sent to the liquid recovery train. In this case, the only liquid product is EG that is then combined with the outlet of the first separator and at 98% or greater purity.

The recycle train of the system begins with a countercurrent heat exchanger followed by an electric heater to elevate the temperature to 200 °C followed by a component splitter set to mimic a hydrogen separating membrane due to the lack of such a unit operation in SuperPro designer. The component splitter is assumed to recover 99% of the hydrogen as reported by available products from Air Liquide. [69] The remaining gas stream is then passed to the shell side of the countercurrent heat exchanger before passing through a butterfly valve to lower the pressure back to just over 1 atm. The stream then passes through a flow splitter used to mimic a purge system. The percentage of the stream that is purged is varied as shown in Table S10 to ensure that the ethylene stream fed to the reactor maintains an ethylene purity of >98% by mass. The remaining gas stream in the recycle loop is then cooled via an electric cooler to 25 °C before combining with the pure ethylene feed to reenter the system.

Table S10. Absorber water requirements and purge percentage requirements for the process model for System E3. Purge percentages are set to maintain a 98% purity of ethylene being fed to the reactor.

Ethylene Single Pass Conversion %	**Purge Percentage**
0.01%	94.2%
10%	95.30%
20%	97.70%
30%	98.40%
40%	98.70%
50%	99.10%
60%	99.20%
70%	99.30%
80%	99.40%
90%	99.50%

S3.4 System E4 Electrochemical Ethylene Epoxidation Process Model

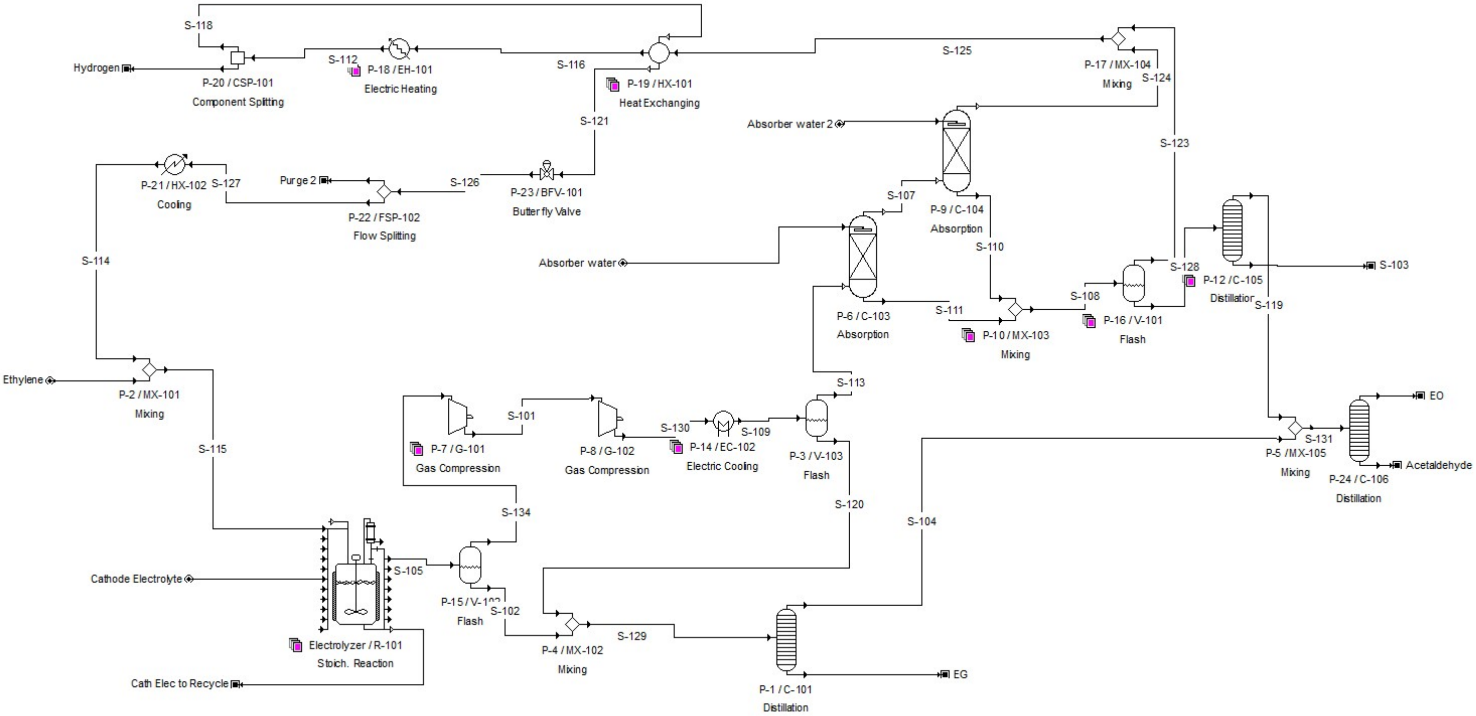

Figure S6. Gaseous ethylene electrooxidation process model flow diagram for literature System E4.

The gaseous ethylene electrooxidation process model for System E4 assumes a 453 ktonnes per year ethylene feed rate at STP. In this model, a premixed water and electrolyte mixture at STP with a 0.1 M $NaClO_4$ concentration is mixed with a previously combined fresh ethylene stream and recycled ethylene stream. This stream is then fed to a stoichiometric reactor assuming carbon selectivities as stated in Table S4 and varied single pass conversion rates as shown in Table S11. A stoichiometric volume of hydrogen is assumed to be produced in this reaction to mimic that of an electrolyzer. The reaction is carried out at STP to mimic the conditions of an electrochemical process. To model the reactor like an electrolyzer, the reactor is set to split the streams with all cathode side products, unreacted ethylene, hydrogen, and oxygen leaving the top of the reactor and the water and electrolyte (anode side) leaving the bottom of the reactor. The anode side

stream recycle is not shown in the figure; however, the cost for this stream is set to zero to account for the potential to recycle the stream.

The cathode side components leaving the reactor for System E4 are ethylene, EO, acetaldehyde, EG, glycolaldehyde, H_2, and O_2. As SuperPro Designer does not have a built in electrolyzer unit operation, we determined energy requirements, maintenance costs, and capital cost of the reactor with an external model created based on the DOE H2A model.[67]

The cathode side stream from the reactor is sent to a flash vessel at 25 °C and 1 bar to recover as much of the liquid stream as possible modeled by Henry's Law in the process design software. The remaining gaseous products from the reactor are compressed via a two-stage compressor system (80% efficiency) with interstage electric cooling to 30 bar. The stream then passes to another separator to remove as much of the liquids as possible to be sent to the liquid recovery train. The compressed gas stream then passes through a first absorption column fed with water at 25 °C at 30 bar at varied required rates shown in Table S11. Under these conditions, 53.15% of the acetaldehyde, 53.15% of the EO, 0.4385% of the ethylene, and 0.02% of the hydrogen is assumed to be absorbed.[68] The unabsorbed gases then pass through a second absorption column with the same assumed absorption percentages to try and recover as much of the products as possible. The bottoms streams from both absorbers are combined and heated to 50 °C where the ethylene and H_2 are released and sent to a recycle train. The liquid stream from the flash vessel passes through a distillation column designed to recover 99.99% of both the acetaldehyde and EO in the distillate with the bottoms containing water. The distillate stream passes through a second distillation column designed to produce >90% by mass purity of EO with acetaldehyde as a bottoms stream.

The liquid stream is then passed to an atmospheric distillation column designed to recover the EO and acetaldehyde from the distillate that is then combined with the distillation from the gas side of the process to recover each product individually. The liquid stream now containing glycolaldehyde and EG is passed to a second atmospheric distillation column to separate the glycolaldehyde as the distillate and EG as the bottoms stream.

The recycle train of the system begins with the mixing of the unabsorbed gases from the absorber train that contains ethylene, unabsorbed EO, unabsorbed acetaldehyde, H_2, and O_2. The stream passes through a countercurrent heat exchanger followed by an electric heater are used to elevate the temperature to 200 °C. The heated stream is then split by a component splitter set to mimic a hydrogen separating membrane due to the lack of such a unit operation in SuperPro designer. The component splitter is assumed to recover 99% of the hydrogen as reported by available products from Air Liquide.[69] The remaining gas stream is then passed to the shell side of the countercurrent heat exchanger before passing through a butterfly valve to lower the pressure back to just over 1 atm. The stream then passes through a flow splitter used to mimic a purge system. The percentage of the stream that is purged is varied as shown in Table S11to ensure that the ethylene stream fed to the reactor maintains an ethylene purity of >98% by mass. The remaining gas stream in the recycle loop is then cooled via an electric cooler to 25 °C before combining with the pure ethylene feed to reenter the system.

Table S11. Absorber water requirements and purge percentage requirements for the process model for System E4. Absorber water volumes are the minimum required flow rates to operate the column. Purge percentages are set to maintain a 98% purity of ethylene being fed to the reactor. Purge percentages are notably higher in this reaction to account for the significantly lower Faradaic efficiency resulting in increased oxygen production not otherwise removed from the recycle loop.

Ethylene Single Pass Conversion %	Absorber 1 Water Requirement (kmol/h)	Absorber 2 Water Requirement (kmol/h)	Purge Percentage
0.01%	15,900	15,900	90.00%
10%	28,700	28,600	93.50%
20%	40,600	40,400	96.70%
30%	52,800	52,600	97.70%
40%	65,100	64,800	98.30%
50%	77,400	77,000	98.70%
60%	89,800	89,300	98.90%
70%	102,200	101,600	99.00%
80%	114,599	113,900	99.20%
90%	126,899	126,100	99.30%

S3.5 Theoretical Electrochemical Ethylene Epoxidation Process Model

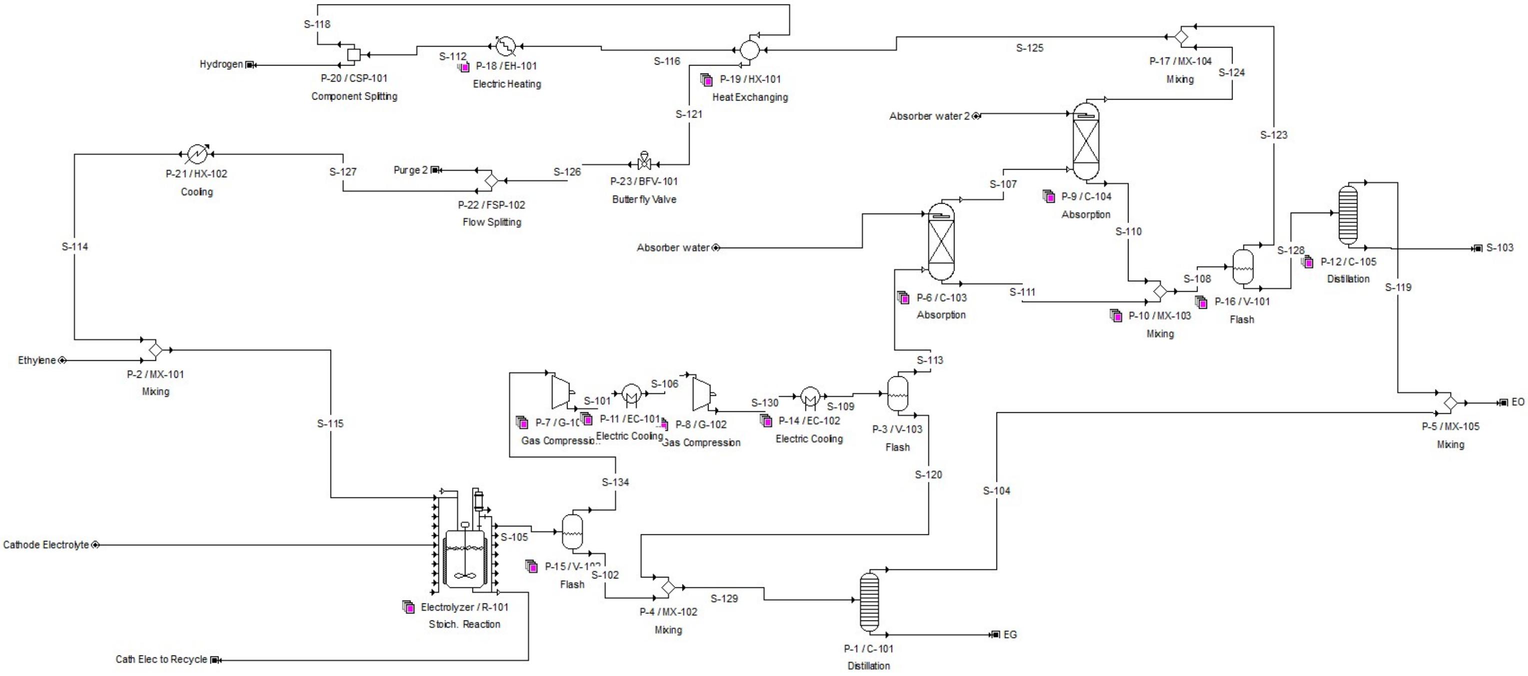

Figure S7. Gaseous ethylene electrooxidation process model flow diagram for theoretical reactions with varied single pass conversions and selectivities for EO versus EG.

The gaseous electrochemical ethylene electrooxidation process models for theoretical reactions with varied single pass conversions and selectivities for EO vs EG assumes a 453 ktonnes per year ethylene feed rate at STP. In this model, water and electrolyte are mixed at STP with a 0.1 M $NaClO_4$ concentration is mixed with a previously combined fresh ethylene stream and recycled ethylene stream. This stream is then fed to a stoichiometric reactor assuming varied carbon selectivities for EO/EG with no other side products outlined in Table S12 and varied single pass conversion rates also shown in Table S12. A stoichiometric volume of hydrogen is assumed to be produced in this reaction to mimic that of an electrolyzer. 100% Faradaic efficiency is assumed in this model to aid in identification of the economically preferred product that can be formed in this theoretical scenario. To model the reactor like an electrolyzer, the reactor is set to split the streams with all cathode side products (EO and/or EG), unreacted ethylene, hydrogen, and oxygen leaving the top of the reactor and the water and electrolyte (anode side) leaving the bottom of the reactor. The anode side stream recycle is not shown in the figure; however, the cost for this stream is set to zero to account for the potential to recycle the stream.

The cathode side components leaving the leaving the reactor are ethylene, EO, EG, H_2, and O_2. As SuperPro Designer does not have a built in electrolyzer unit operation, we determined energy requirements, maintenance costs, and capital cost of the reactor with an external model based on the DOE H2A model.[67]

The cathode side stream from the reactor is sent to a flash vessel at 25 °C and 1 bar to recover as much of the liquid stream as possible modeled by Henry's Law in the process design software. The remaining gaseous products from the reactor are compressed via a two-stage compressor system (80% efficiency) with interstage electric cooling to 30 bar. The stream then passes to another separator to remove as much of the liquids as possible to be sent to the liquid recovery train. The compressed gas stream then passes through a first absorption column fed with water at 25 °C at 30 bar at varied required rates shown in Table S12. Under these conditions, 53.15% of the acetaldehyde, 53.15% of the EO, 0.4385% of the ethylene, and 0.02% of the hydrogen is assumed to be absorbed.[68] The unabsorbed gases then pass through a second absorption column with the same assumed absorption percentages to try and recover as much of the products as possible. The bottoms streams from both absorbers are combined and heated to 50 °C where the ethylene and H_2 are released and sent to a recycle train. The liquid stream from the flash vessel passes through a distillation column designed to recover 99.99% of the EO in the distillate with the bottoms containing water.

The liquid stream is then passed to an atmospheric distillation column designed to recover the EO from the distillate and the EG from the bottoms stream.

The recycle train of the system begins with the mixing of the unabsorbed gases from the absorber train that contains ethylene, unabsorbed EO, unabsorbed acetaldehyde, H_2, and O_2 The stream passes through a countercurrent heat exchanger followed by an electric heater are used to elevate the temperature to 200 °C. The heated stream is then split by a component splitter set to mimic a hydrogen separating membrane due to the lack of such a unit operation in SuperPro designer. The component splitter is assumed to recover 99% of the hydrogen as reported by available products from Air Liquide.[69] The remaining gas stream is then passed to the shell side of the countercurrent heat exchanger before passing through a butterfly valve to lower the pressure back to just over 1 atm. The stream then passes through a flow splitter used to mimic a purge system. The percentage of the stream that is purged is varied as shown in Table S12 to ensure that the ethylene stream fed to the reactor maintains an ethylene purity of >98% by mass. The remaining gas stream in the recycle loop is then cooled via an electric cooler to 25 °C before combining with the pure ethylene feed to reenter the system.

Table S12. Absorber water requirements and purge percentage requirements for the process models for theoretical reactions with varied single pass conversions and selectivities for EO versus EG. Absorber water volumes are the minimum required flow rates to operate the column. Purge percentages are set to maintain a 98% purity of ethylene being fed to the reactor. Purge percentages are notably higher in this reaction to account for the significantly lower Faradaic efficiency resulting in increased oxygen production not otherwise removed from the recycle loop.

Selectivity for EO/Selectivity for EG	Ethylene Single Pass Conversion %	Absorber 1 Water Requirement (kmol/h)	Absorber 2 Water Requirement (kmol/h)	Purge Percentage
100% EO 0% EG	10%	27,200	25,600	47.7%
	20%	18,300	16,400	72.3%
	30%	16,300	13,800	81.1%
	40%	15,400	12,200	85.7%
	50%	14,800	11,000	88.5%
	60%	14,400	9,900	90.4%
	70%	14,100	8,910	91.7%
	80%	13,800	8,000	92.8%
	90%	13,600	7,200	93.6%
90% EO 10% EG	10%	79,800	77,300	12.5%
	20%	50,900	49,300	21.3%
	30%	41,400	31,200	28.6%
	40%	37,300	36,200	34.2%
	50%	35,000	34,000	39.7%
	60%	34,000	33,000	43.7%
	70%	33,500	32,500	47.5%
	80%	33,400	32,400	50.5%
	90%	33,500	33,200	54.0%
80% EO 20% EG	10%	80,500	78,000	12.3%
	20%	51,000	49,400	21.2%
	30%	41,500	40,200	28.5%
	40%	37,400	36,200	34.2%
	50%	35,100	34,100	39.4%
	60%	34,000	33,000	43.8%
	70%	33,500	32,500	47.3%
	80%	33,400	32,400	50.7%
	90%	33,500	32,500	53.6%
70% EO	10%	81,800	79,300	11.9%

Selectivity for EO/Selectivity for EG	Ethylene Single Pass Conversion %	Absorber 1 Water Requirement (kmol/h)	Absorber 2 Water Requirement (kmol/h)	Purge Percentage
30% EG	20%	51,100	49,500	21.1%
	30%	41,600	40,300	28.3%
	40%	37,300	36,200	34.2%
	50%	35,100	34,100	39.2%
	60%	34,000	33,000	43.5%
	70%	33,500	32,500	47.3%
	80%	33,400	32,400	50.7%
	90%	33,500	32,600	53.4%
60% EO 40% EG	10%	87,100	84,400	10.5%
	20%	51,100	49,500	21.1%
	30%	41,600	40,400	28.2%
	40%	37,300	36,200	34.2%
	50%	35,100	34,100	39.2%
	60%	34,000	33,000	43.5%
	70%	33,500	32,500	47.3%
	80%	33,400	32,400	50.7%
	90%	33,500	32,600	53.4%
50% EO 50% EG	10%	142,800	138,700	2.0%
	20%	51,300	49,700	20.9%
	30%	41,600	40,400	28.2%
	40%	37,300	26,200	34.2%
	50%	35,100	34,100	39.2%
	60%	34,000	33,000	43.5%
	70%	33,500	32,500	47.2%
	80%	33,400	32,400	50.5%
	90%	33,500	32,600	53.4%
40% EO 60% EG	10%	159,710	155,900	0.5%
	20%	51,800	50,200	20.4%
	30%	41,700	40,500	28.0%
	40%	37,310	36,200	34.1%
	50%	35,200	34,100	39.1%
	60%	34,000	33,000	43.4%
	70%	33,500	32,500	47.2%
	80%	33,400	32,400	50.5%
	90%	33,500	32,600	53.4%
30% EO 70% EG	10%	165,200	162,000	0.01%
	20%	63,100	61,300	12.1%
	30%	42,100	40,800	27.4%
	40%	37,400	36,300	33.9%
	50%	35,200	34,200	39.0%
	60%	34,000	33,000	43.4%

Selectivity for EO/Selectivity for EG	**Ethylene Single Pass Conversion %**	**Absorber 1 Water Requirement (kmol/h)**	**Absorber 2 Water Requirement (kmol/h)**	**Purge Percentage**
	70%	33,500	32,510	47.1%
	80%	33,400	32,400	50.4%
	90%	33,500	32,510	53.3%
20% EO 80% EG	10%	163,500	161300	0.01%
	20%	92,200	90,300	0.01%
	30%	55,500	54,100	9.90%
	40%	40,000	38,900	27.00%
	50%	35,700	34,600	36.90%
	60%	34,200	33,200	42.50%
	70%	33,510	32,600	46.70%
	80%	33,400	32,400	50.10%
	90%	33,500	32,500	53.30%
10% EO 90% EG	10%	161,900	160,500	0.01%
	20%	90,600	89,600	0.01%
	30%	66,800	65,900	0.01%
	40%	54,900	54,000	0.01%
	50%	47,700	46,900	0.01%
	60%	41,900	41,100	3.80%
	70%	37,200	26,500	14.10%
	80%	34,900	34,200	22.50%
	90%	33,800	33,100	29.20%

S3.6 Theoretical Electrochemical Ethylene Epoxidation Process Model

Table S13. Summary of highest performing literature ethylene epoxidation reaction systems under theoretical single pass conversions. Bold and white cells indicate exceeding the top ethylene value, while grey cells indicate an NPV per kg$_{\text{ethylene}}$ below this value.

System	Single Pass Conversion	First Quartile (NPV/kg$_{\text{ethylene}}$)	Median (NPV/kg$_{\text{ethylene}}$)	Third Quartile (NPV/kg$_{\text{ethylene}}$)
Ethylene Market Value		**$0.83 - $1.50**		
E1	90%	$1.02	**$3.22**	**$5.17**
	80%	-$0.19	**$1.91**	**$3.83**
	70%	-$1.46	$0.55	**$2.43**
E2	90%	-$0.09	**$2.08**	**$4.03**
	80%	-$1.55	$0.50	**$2.40**
	70%	-$3.08	-$1.15	$0.71
E3	**90%**	**$3.74**	**$6.65**	**$9.30**
	80%	**$1.96**	**$4.64**	**$7.05**
	70%	$0.14	**$2.60**	**$4.81**
E4	90%	-$6.14	-$3.52	-$1.10

S3.7 System E3 Sensitivity to Applied Voltage and Electricity Price

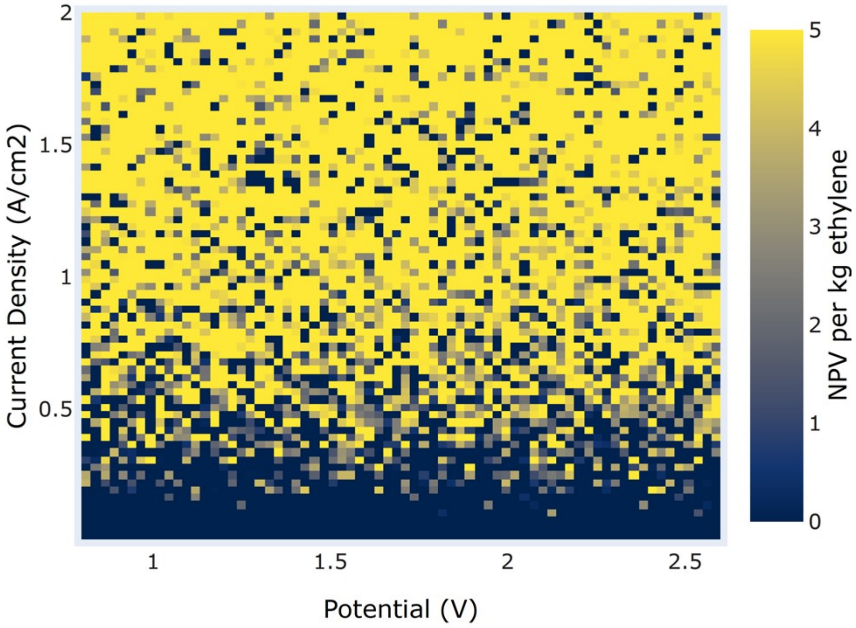

Figure S8. NPV per kg of ethylene for System E3 carbon selectivities against applied voltage and current density at observed literature single pass conversion and modeled single pass conversions. Uncertainty is incorporated in the heat map by utilizing data from all 800,000 simulations and taking the mean value in each pixel to signify the region in which, under uncertainty, the electrochemical process is economically feasible.

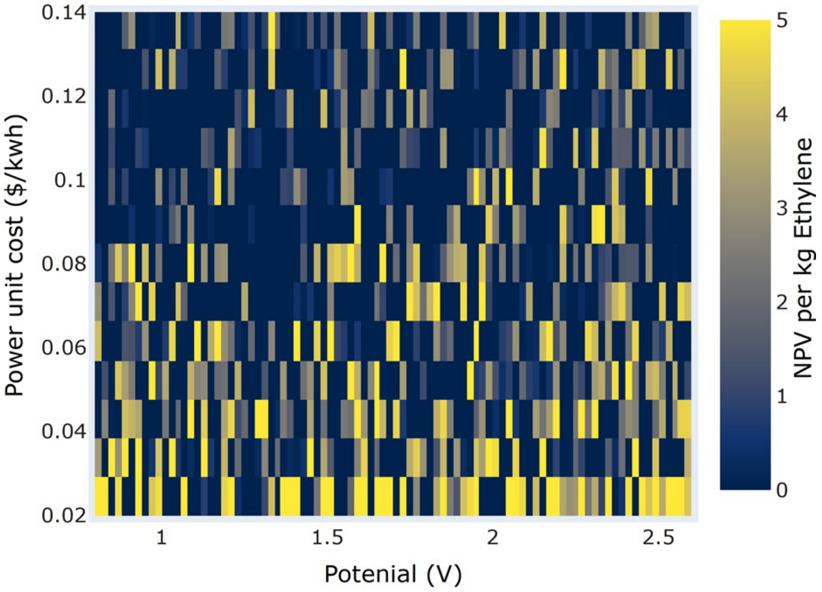

Figure S9. NPV per kg of ethylene for System E3 carbon selectivities against applied voltage and electricity price at observed literature single pass conversion and modeled single pass conversions. Uncertainty is incorporated in the heat map by utilizing data from all 800,000 simulations and taking the mean value in each pixel to signify the region in which, under uncertainty, the electrochemical process is economically feasible.

S4. Gaseous Electrochemical Propylene Epoxidation Process Models and Additional Results Summaries

S4.1 System P1, P2, and P3 Electrochemical Propylene Epoxidation Process Model

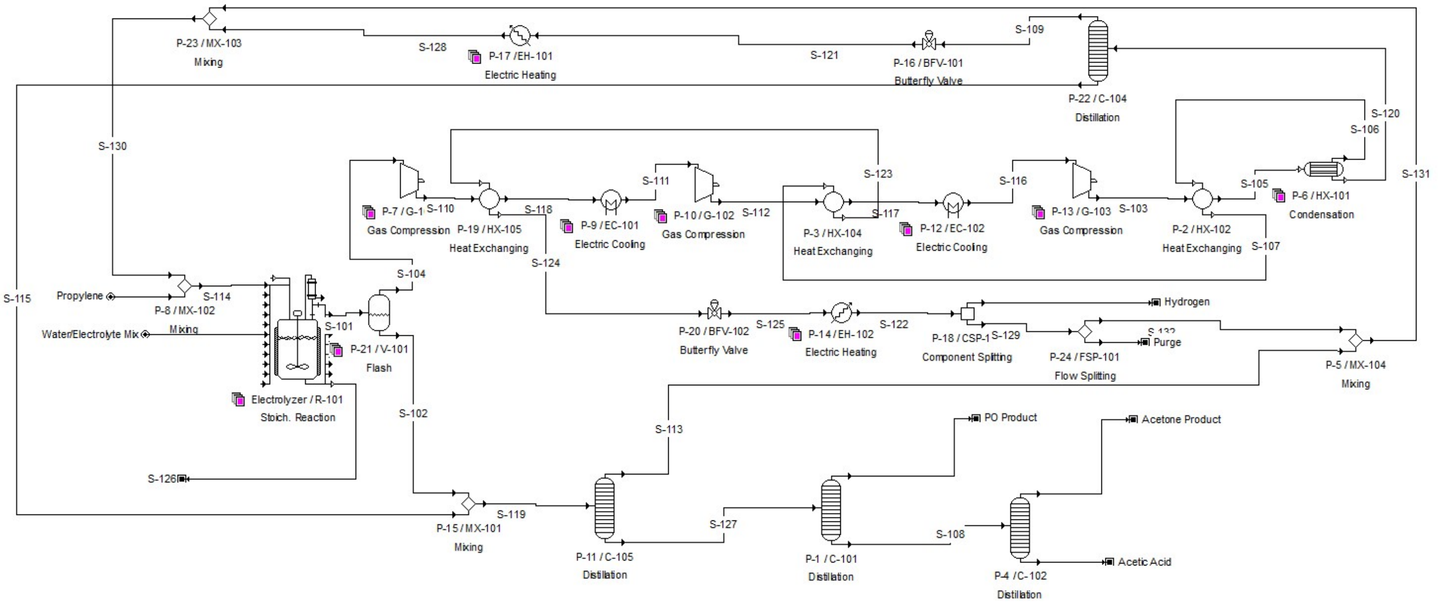

Figure S10. Gaseous propylene electrooxidation process model flow diagram in for literature System P1, P2, and P3.

The gaseous electrochemical propylene electrooxidation process model for System P1, P2, and P3 assumes a 181 ktonnes per year propylene feed rate at STP. In this model, a premixed water and electrolyte mixture at STP with a 0.1 M phosphate buffer (modeled as K_2HPO_4) concentration is mixed with a previously combined fresh propylene stream and recycled propylene stream. This stream is then fed to a stoichiometric reactor assuming carbon selectivities as stated in Table S5 and varied single pass conversion rates as shown in Table S14. The three reactions in this case utilize the same model with modification to the reactor to accommodate the respective selectivities for each System, P1, P2, or P3. A stoichiometric volume of hydrogen is assumed to be produced in this reaction to mimic that of an electrolyzer.

The reaction is carried out at STP to mimic the conditions of an electrochemical process. To model the reactor like an electrolyzer, the reactor is set to split the streams with all cathode side products, unreacted propylene, hydrogen, and oxygen leaving the top of the reactor and the water and electrolyte (anode side) leaving the bottom of the reactor. The anode side stream recycle is not shown in the figure; however, the cost for this stream is set to zero to account for the potential to recycle the stream.

The cathode side components leaving the reactor are propylene, PO, acetic acid, acetone, H_2, and O_2. As SuperPro Designer does not have a built in electrolyzer unit operation, we determined energy requirements, maintenance costs, and capital cost of the reactor with an external model based on the DOE H2A model.[67]

The cathode side stream from the reactor is sent to a flash vessel at 25 °C and 1 bar to recover as much of the liquid stream as possible modeled by Henry's Law in the process design software.

The gaseous products from the reactor are compressed via a three-stage compressor system (80% efficiency) outlet to varied pressures depending on the single pass conversion outlined in Table S14 to maximize the recovery of the unreacted propylene with interstage electric cooling, and interstage shell and tube exchangers coming from the condenser outlet. The compressed gas stream then passes through a condenser set to -10 °C cooled by $CaCl_2$ brine to liquify the propylene, and residual PO in the stream that is then separated in a distillation column to separate the propylene in the distillate and send the PO rich stream bottoms to the liquids recovery section. The pressure in the liquid propylene stream is lowered to 1 atm through a valve and reheated/regassified by an electric heater to 25 °C and is combined with the fresh propylene stream. The uncondensed gases from the condenser including some propylene, H_2, and O_2 are reheated through the shell sides of the heat exchangers in the compression system. The pressure is lowered to 30 bar and the gas is heated to 200 °C by an electric heater and then enters a component splitter set to mimic a hydrogen separating membrane due to the lack of such a unit operation in SuperPro designer. The component splitter is assumed to recover 99% of the hydrogen as reported by available products from Air Liquide [69]. The remaining gas stream containing unrecovered propylene and H_2 and O_2 is then purged.

This liquid stream from the first separator is passed to a distillation column set to 20 bar designed to recover 99.9% of the propylene as the distillate, as the VLE leads to some carry over of the unreacted propylene into the liquid separation portion of the facility. The bottoms stream of the distillation column contains PO, acetic acid, and acetone. The bottoms stream passes to an atmospheric distillation column designed to recover 99.9% of the PO. The bottoms streams containing acetic acid and acetone then passes to a third atmospheric distillation column to separate the two products.

Table S14. Recycle system compression train setting at the condenser for the process model for Systems P1, P2, and P3.

Propylene Single Pass Conversion %	System P1 Purge Percentage	System P2 Purge Percentage	System P3 Purge Percentage
10%	88.6%	89.9%	91.8%
11.4%	89.9%	N/A	N/A
12.4%	N/A	N/A	93.1%
14.1%	N/A	92.6%	N/A
20%	94.0%	94.7%	95.7%
30%	95.9%	96.4%	97.1%
40%	96.9%	97.3%	97.9%
50%	97.5%	97.8%	98.3%
60%	98.0%	98.2%	98.6%
70%	98.2%	98.5%	98.8%
80%	98.5%	98.7%	98.9%
90%	98.6%	98.8%	99.0%

Propylene Single Pass Conversion %	System P1 Pressure at the Condenser (bar)	System P2 Pressure at the Condenser (bar)	System P3 Pressure at the Condenser (bar)
10%	30	30	40
11.4%	35	N/A	N/A
12.4%	N/A	N/A	43
14.1%	N/A	37	N/A
20%	50	50	65
30%	75	75	90
40%	100	100	115
50%	125	125	140
60%	150	150	170
70%	180	180	195
80%	210	210	210
90%	240	240	245

S4.2 System P4 Electrochemical Propylene Epoxidation Process Model

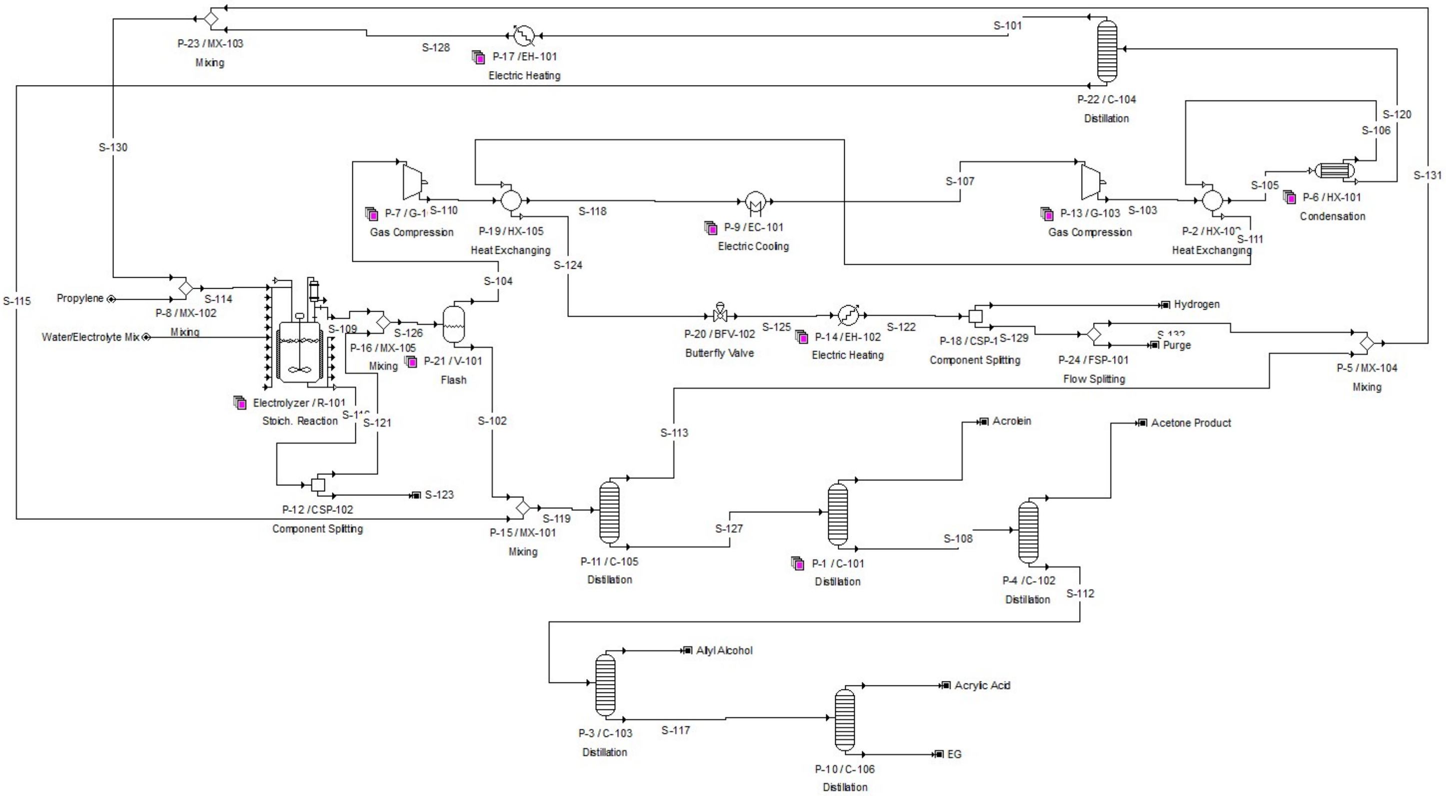

Figure S11. Gaseous propylene electrooxidation process model flow diagram for literature System P4.

The gaseous propylene electrooxidation process model for System P4 assumes a 181 ktonnes propylene feed rate at STP. In this model, a premixed water and electrolyte mixture at STP with a 0.1 M perchloric acid concentration is mixed with a previously combined fresh propylene stream and recycled propylene stream. This stream is then fed to a stoichiometric reactor assuming carbon selectivities as stated in Table S5 and varied single pass conversion rates as shown in Table S15 A stoichiometric volume of hydrogen is assumed to be produced in this reaction to mimic that of an electrolyzer. The reaction is carried out at STP to mimic the conditions of an electrochemical process. To model the reactor like an electrolyzer, the reactor is set to split the streams with all cathode side products, unreacted propylene, hydrogen, and oxygen leaving the top of the reactor and the water and electrolyte (anode side) leaving the bottom of the reactor. The anode side stream recycle is not shown in the figure; however, the cost for this stream is set to zero to account for the potential to recycle the stream.

The cathode side components leaving the reactor are propylene, PG, acrolein, acetone, allyl alcohol, acrylic acid, H_2, and O_2. As SuperPro Designer does not have a built in electrolyzer unit operation, we determined energy requirements, maintenance costs, and capital cost of the reactor with an external model based on the DOE H2A model.[67]

The cathode side stream from the reactor is sent to a flash vessel at 25 °C and 1 bar to recover as much of the liquid stream as possible modeled by Henry's Law in the process design software.

The gaseous products from the reactor are compressed via a compressor system (80% efficiency) outlet to varied pressures depending on the single pass conversion outlined in Table S15 to maximize the recovery of the unreacted propylene with interstage electric cooling, and interstage shell and tube exchangers coming from the condenser outlet. The compressed gas stream then passes through a condenser set to -10 °C cooled by $CaCl_2$ brine to liquify the propylene, and residual products in the stream that is then separated in a distillation column to separate the propylene in the distillate and send the liquid stream bottoms to the liquids recovery section. The pressure in the liquid propylene stream is lowered to 1 atm through a valve and reheated/regassified by an electric heater to 25 °C and is combined with the fresh propylene stream. The uncondensed gases from the condenser including some propylene, H_2 and O_2 are reheated through the shell sides of the heat exchangers in the compression system. The pressure is lowered to 30 bar and the gas is heated to 200 °C by an electric heater and then enters a component splitter set to mimic a hydrogen separating membrane due to the lack of such a unit operation in SuperPro designer. The component splitter is assumed to recover 99% of the hydrogen as reported by available products from Air Liquide [69]. The remaining gas stream containing unrecovered propylene and H_2 and O_2 is then purged.

This liquid stream from the first separator is passed to a distillation column set to 20 bar designed to recover 99.9% of the propylene as the distillate, as the VLE leads to some carry over of the unreacted propylene into the liquid separation portion of the facility. The bottoms stream of the distillation column is then passed through a series of distillation columns to individually recover each of the PG, acrolein, acetone, allyl alcohol, acrylic acid products.

Table S15. Recycle system compression train setting at the condenser for the process model for System P4.

Propylene Single Pass Conversion %	**System 4 Purge Percentage**	**System P4 Pressure at the Condenser (bar)**
0.01%	51.0%	10
10%	66.0%	20
20%	79.5%	40
30%	85.5%	60
40%	88.7%	80
50%	90.8%	100
60%	92.2%	120
70%	93.2%	150
80%	94.1%	180
90%	94.7%	210

S4.3 Theoretical Electrochemical Propylene Epoxidation Process Model

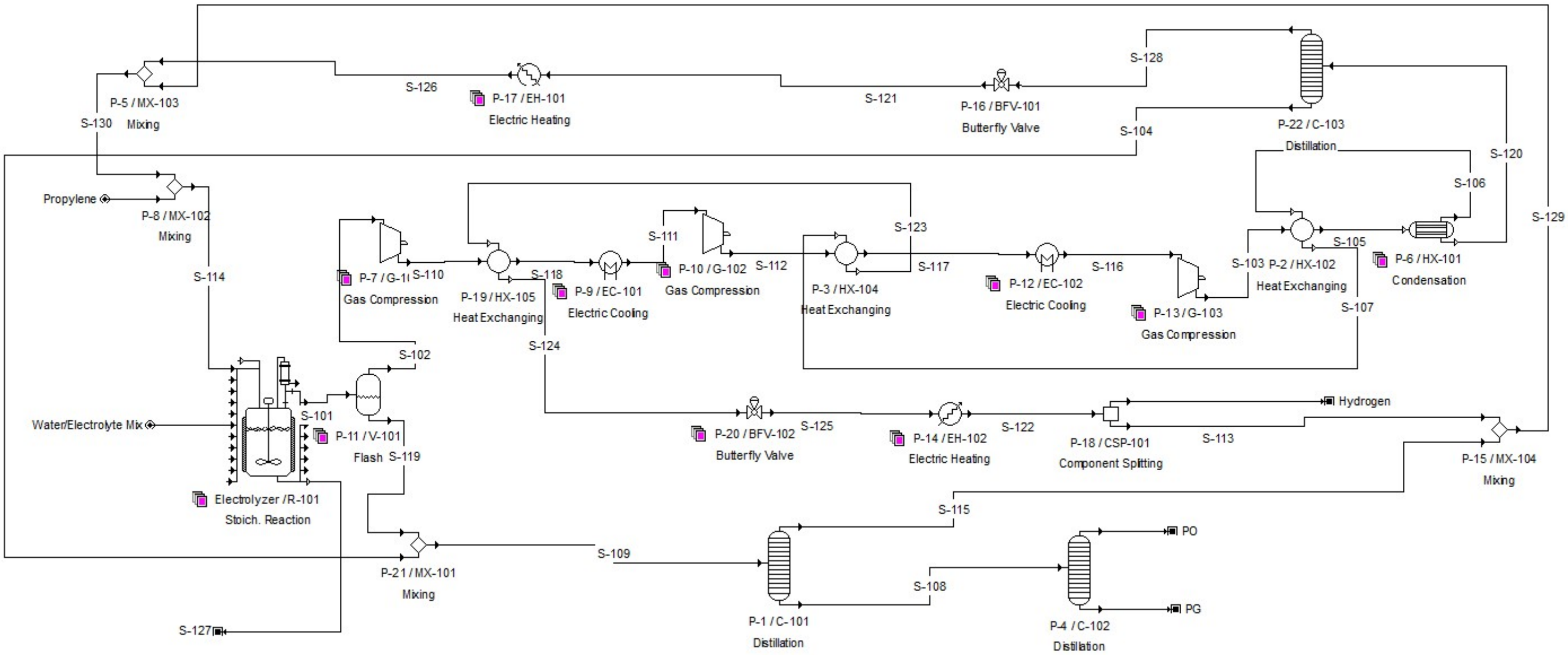

Figure S12. Gaseous propylene electrooxidation process model flow diagram for theoretical reactions with varied single pass conversions and selectivities for PO versus PG.

The gaseous propylene electrooxidation process model for theoretical reactions with varied single pass conversions and selectivities for PO versus PG assumes a 181 ktonnes propylene feed rate at STP. In this model, a premixed water and electrolyte mixture at STP with a 0.1 M phosphate buffer (modeled as K_2HPO_4) concentration is mixed with a previously combined fresh propylene stream and recycled propylene stream. This stream is then fed to a stoichiometric reactor assuming varied carbon selectivities for PO and PG with no other side products formed at varied single pass conversion rates as shown in Table S16. A stoichiometric volume of hydrogen is assumed to be produced in this reaction to mimic that of an electrolyzer. The reaction is carried out at STP to mimic the conditions of an electrochemical process. To model the reactor like an electrolyzer, the reactor is set to split the streams with all cathode side products, unreacted propylene, hydrogen, and oxygen leaving the top of the reactor and the water and electrolyte (anode side) leaving the bottom of the reactor. The anode side stream recycle is not shown in the figure; however, the cost for this stream is set to zero to account for the potential to recycle the stream.

The cathode side components leaving the reactor are propylene, PO, PG, H_2, and O_2. As SuperPro Designer does not have a built in electrolyzer unit operation, we determined energy requirements, maintenance costs, and capital cost of the reactor with an external model based on the DOE H2A model.[67]

The cathode side stream from the reactor is sent to a flash vessel at 25 °C and 1 bar to recover as much of the liquid stream as possible modeled by Henry's Law in the process design software.

The gaseous products from the reactor are compressed via a compressor system (80% efficiency) outlet to varied pressures depending on the single pass conversion outlined in Table S16 to maximize the recovery of the unreacted propylene with interstage electric cooling, and interstage shell and tube exchangers coming from the condenser outlet. The compressed gas stream then passes through a condenser set to -10 °C cooled by $CaCl_2$ brine to liquify the propylene, and residual products in the stream that is then separated in a distillation column to separate the propylene in the distillate and send the liquid stream bottoms to the liquids recovery section. The pressure in the liquid propylene stream is lowered to 1 atm through a valve and reheated/regassified by an electric heater to 25 °C and is combined with the fresh propylene stream. The uncondensed gases from the condenser including some propylene, H_2, and O_2 are reheated through the shell sides of the heat exchangers in the compression system. The pressure is lowered to 30 bar and the gas is heated to 200 °C by an electric heater and then enters a component splitter set to mimic a hydrogen separating membrane due to the lack of such a unit operation in SuperPro designer. The component splitter is assumed to recover 99% of the hydrogen as reported by available products from Air Liquide [69]. The remaining gas stream containing unrecovered propylene and H_2 and O_2 is then purged.

This liquid stream from the first separator is passed to a distillation column set to 20 bar designed to recover 99.9% of the propylene as the distillate, as the VLE leads to some carry over of the unreacted propylene into the liquid separation portion of the facility. The bottoms stream of the distillation column then separates and recovers the PO as the distillate and PG as the bottoms stream.

Table S16. Recycle system compression train setting at the condenser for the process model for theoretical reactions with varied single pass conversions and selectivities for PO versus PG.

Selectivity for PO/Selectivity for PG	Propylene Single Pass Conversion %	Pressure at the Condenser (bar))
100% PO 0% PG	10%	15
	20%	25
	30%	40
	40%	55
	50%	65
	60%	75
	70%	85
	80%	95
	90%	105
90% PO 10% PG	10%	15
	20%	25
	30%	40
	40%	55
	50%	70
	60%	85
	70%	100
	80%	110
	90%	165
80% PO 20% PG	10%	15
	20%	25
	30%	40
	40%	55
	50%	70
	60%	90
	70%	110
	80%	135
	90%	165
70% PO 30% PG	10%	15
	20%	25
	30%	40
	40%	55
	50%	70
	60%	90
	70%	110
	80%	135
	90%	165
60% PO	10%	15

Selectivity for PO/Selectivity for PG	Propylene Single Pass Conversion %	Pressure at the Condenser (bar))
40% PG	20%	25
	30%	40
	40%	65
	50%	90
	60%	115
	70%	150
	80%	190
	90%	230
50% PO 50% PG	10%	15
	20%	25
	30%	40
	40%	65
	50%	100
	60%	135
	70%	175
	80%	275
	90%	300
40% PO 60% PG	10%	15
	20%	25
	30%	40
	40%	65
	50%	100
	60%	130
	70%	175
	80%	275
	90%	475
30% PO 70% PG	10%	15
	20%	25
	30%	40
	40%	65
	50%	100
	60%	125
	70%	175
	80%	275
	90%	475
20% PO 80% PG	10%	15
	20%	25
	30%	40
	40%	65
	50%	100
	60%	125

Selectivity for PO/Selectivity for PG	Propylene Single Pass Conversion %	Pressure at the Condenser (bar))
	70%	175
	80%	275
	90%	475
10% PO 90% PG	10%	15
	20%	25
	30%	40
	40%	65
	50%	100
	60%	125
	70%	175
	80%	275
	90%	475

S4.4 System P2 Sensitivity to Applied Voltage and Electricity Price

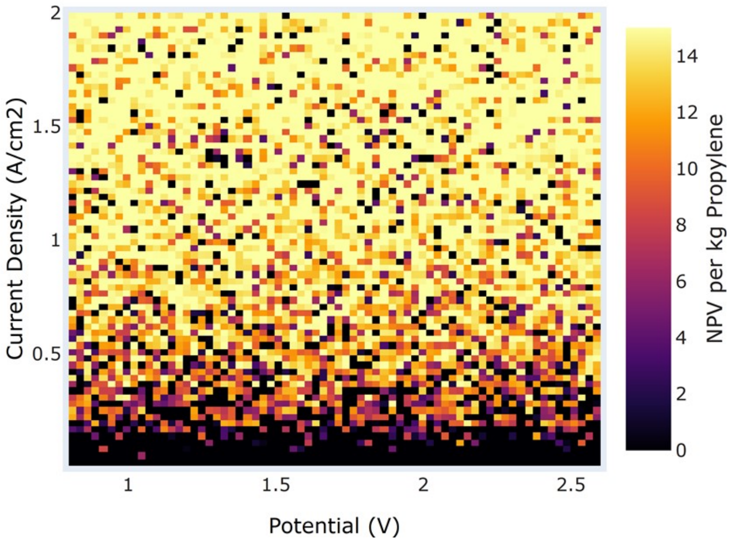

Figure S13. NPV per kg of propylene for System P2 carbon selectivities against applied voltage and current density at 90% single pass conversion. Uncertainty is incorporated in the heat map by utilizing data from all 800,000 simulations and taking the mean value in each pixel to signify the region in which, under uncertainty, the electrochemical process is economically feasible

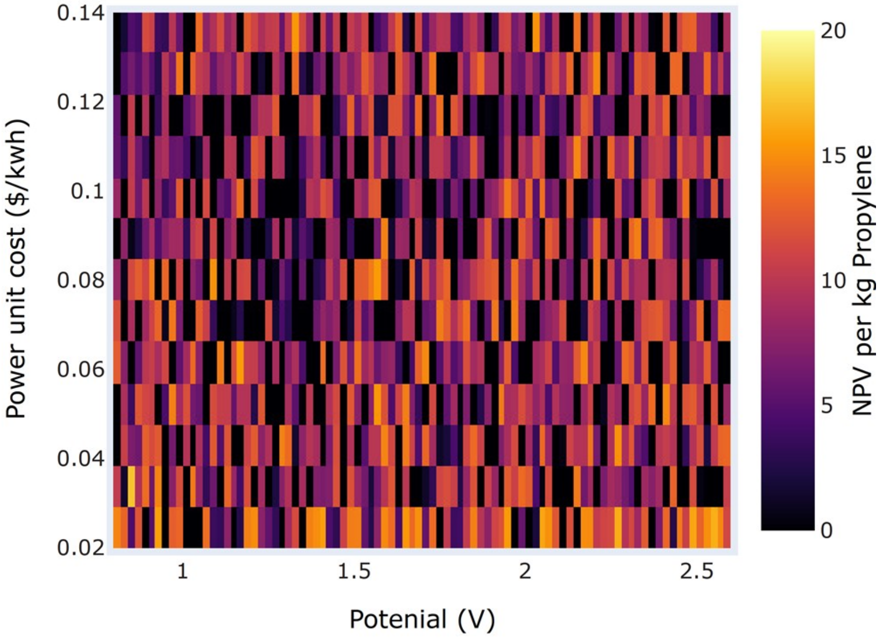

Figure S14. NPV per kg of propylene for System P2 carbon selectivities against applied voltage and electricity price at 90% single pass conversion. Uncertainty is incorporated in the heat map by utilizing data from all 800,000 simulations and taking the mean value in each pixel to signify the region in which, under uncertainty, the electrochemical process is economically feasible.

S5. Uncertainty Analysis Parameters

S5.1 Ethylene Processes Uncertainty Analysis Parameters

Table S17. Parameters varied in the economic model's uncertainty analysis and their respective values for the gaseous ethylene electrooxidation models.

Model Parameter	**Value Range**	**Distribution Type**	**Source**
Faradaic Efficiency	0.01-99.99%	Uniform	Assumed range
Potential (V)	0.8–2.6	Uniform	Assumed range
Current Density (A/cm^2)	0.001-2.000	Uniform	Assumed range
Electrolyzer cost per m^2	\$5,000-\$20,0000	Uniform	67
Electrolyzer Installation Costs Percentage of Capital Costs	8%-16% Note: 10% is the installation factor utilized in the H2A Model	Uniform	67
Labor Rate (\$/hr)	\$55.20-\$82.80	Uniform	+/- 20% from default SuperPro Designer base value
Ethylene Cost (\$/kg)	\$0.83-\$1.50	Uniform	70
Water Cost (\$/kgal)	Average: \$3.95 STD: \$1.10	Normal	71
Power unit cost (\$/kWh)	\$0.02-\$0.14	Uniform	+/- 20% from default SuperPro Designer base value
Steam Unit Cost (\$/MT)	\$10-\$14	Uniform	+/- 20% from default SuperPro Designer base value
HP Steam Unit Cost (\$/MT)	\$16-\$24	Uniform	+/- 20% from default SuperPro Designer base value
Cooling Water Unit Cost (\$/MT)	\$0.02-\$0.10	Uniform	+/- 20% from default SuperPro Designer base value
Chilled Water Costs (\$/MT)	\$0.30-\$0.49	Uniform	+/- 20% from default SuperPro Designer base value
Hot water costs (\$/Mt)	\$0.04-\$0.06	Uniform	+/- \$0.01 from default SuperPro Designer base value
EO Sale Price (\$/kg)	\$1.62-\$1.93	Uniform	72
H2 Sale Price (\$/kg)	\$1.00-\$2.50	Uniform	73
EG Sale Price (\$/kg)	\$0.83-\$1.00	Uniform	74
GA Sale Price (\$/kg)	\$0.77-\$0.93	Uniform	+/- 10% from [75]
Acetaldehyde Sale Price (\$/kg)	\$0.59-\$2.40	Uniform	76
Formic Acid sale price (\$/kg)	\$0.80-\$1.20	Uniform	77
Nominal Tax Rate	25% average	Normal	78
Electrolyzer Replacement Cost % of CAPEX	10%-35%	Uniform	67 Note: 15% is used in the H2A model for PEM electrolyzers. A potentially higher bound is studied here to account for application of a less certain technology
Lifetime of Electrolyzer (yrs)	1 month – 15 years	Uniform	Assumed range

S5.2 Propylene Processes Uncertainty Analysis Parameters

Table S18. Parameters varied in the economic model's uncertainty analysis and their respective values for the gaseous propylene electrooxidation models.

Model Parameter	**Value Range**	**Distribution Type**	**Source**
Faradaic Efficiency	0.01-99.99%	Uniform	Assumed range
Potential (V)	0.8–2.6	Uniform	Assumed range
Current Density (A/cm^2)	0.001-2.000	Uniform	Assumed rang
Electrolyzer cost per m^2	\$5,000-\$20,0000	Uniform	67
Electrolyzer Installation Costs Percentage of Capital Costs	8%-16% Note: 10% is the installation factor utilized in the H2A Model	Uniform	67
Labor Rate (\$/hr)	\$55.20-\$82.80	Uniform	+/- 20% from default SuperPro Designer base value
Propylene Cost (\$/kg)	\$0.52-\$1.64	Uniform	79 79
Water Cost (\$/kgal)	Average: \$3.95 STD: \$1.10	Normal	71
Power unit cost (\$/kWh)	\$0.02-\$0.14	Uniform	+/- 20% from default SuperPro Designer base value
Steam Unit Cost (\$/MT)	\$10-\$14	Uniform	+/- 20% from default SuperPro Designer base value
HP Steam Unit Cost (\$/MT)	\$16-\$24	Uniform	+/- 20% from default SuperPro Designer base value
Cooling Water Unit Cost (\$/MT)	\$0.02-\$0.10	Uniform	+/- 20% from default SuperPro Designer base value
$CaCl_2$ Brine Unit Cost (\$/MT)	\$0.20-\$0.30	Uniform	+/- 20% from default SuperPro Designer base value
Hot Water Unit Cost	\$0.04-\$0.06	Uniform	+/- \$0.01 from default SuperPro Designer base value
PO Sale Price (\$/kg)	\$2.60-\$3.72	Uniform	80
H_2 Sale Price (\$/kg)	\$1.00-\$2.50	Uniform	73
PG Sale Price (\$/kg)	\$1.28-\$3.14	Uniform	81
Acetone Sale Price (\$/kg)	\$0.79-2.03	Uniform	82
Acetic Acid Sale Price (\$/kg)	\$0.66-\$0.90	Uniform	83
Acrolein Sale Price (\$/kg)	\$1.41-\$2.80	Uniform	84
Allyl Alcohol Sale Price (\$/kg)	\$2.20-\$3.20	Uniform	85
Acrylic Acid Sale Price	\$0.99-\$2.23	Uniform	86
Nominal Tax Rate	25% average	Normal	78
Electrolyzer Replacement Cost % of CAPEX	10%-35%	Uniform	67 Note: 15% is used in the H2A model for PEM electrolyzers. A potentially higher bound is studied here to account for application of a less certain technology
Lifetime of Electrolyzer (yrs)	1 month – 15 years	Uniform	Assumed range

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