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Coupling electrocatalytic CO₂ reduction with thermocatalysis enables the formation of a lactone monomer

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Abstract: Carbonylation reactions that generate high-value chemical feedstocks are integral to the formation of many industrially significant compounds. However, these processes require the use of CO, which is invariably derived from fossil-fuel-reforming reactions. CO may also be generated through the electroreduction of CO₂, but the coupling of these two processes is yet to be considered. Merging electrocatalytic reduction of CO₂ to CO with thermocatalytic use of CO would expand the range of the chemicals produced from CO₂. This work describes for the first time the development of a system coupling a high-pressure CO₂ electrolytic cell containing a bimetallic ZnAg catalyst at the cathode for production of CO with a reactor with a faradaic efficiency of >90 % where high pressure CO is used for carbonylating propylene oxide into β -butyrolactone by thermal catalysis, the latter step having a reaction yield above 80%. While the production of monomers and polymers from CO₂ is currently limited to organic carbonates, this strategy opens up the access to lactones from CO₂, for the formation of polyesters.

Introduction

While power generation can be partially 'decarbonized' via electrification, the chemical value chain faces the challenge of a massive 'defossilization' to reach a carbon neutrality in the coming decades. This means that renewable carbon sources, such as CO₂, should be utilized as a carbon feedstock to replace petrochemicals.^[1] Bulk and fine chemicals contain carbon atoms in a variety of oxidation states ranging from +IV (in CO₂ and carbonates) to -III (in alkyl chains). However current processes developed at scale in the industry rely on the functionalization of CO₂ in redox neutral transformations and cover a very narrow scope of chemicals such as cyclic and polymeric carbonates, urea, as well as salicylic acid. The production of the full spectrum of useful chemicals from CO₂, instead, requires the elaboration of transformation sequences able to couple the reduction of CO₂ with its functionalization, in a Power-To-X approach.^[2] The intermediate use of green hydrogen, produced from water electrolysis using low carbon electricity, has been demonstrated in pre-industrial setups for the reduction of CO₂ to formic acid, methanol and methane (Figure 1). The present work explores how an alternative 'power molecule', CO, can be used in a Power-To-Chemical route to couple the reduction of CO₂ by electrocatalysis with a thermocatalytic functionalization of an epoxide, to generate a lactone derivative by exploiting the reactivity of the CO

intermediate. This approach has the potential to unlock the formation of useful esters, amides, etc. from CO₂.^[3] Indeed, energizing CO₂ in the form of CO allows the introduction of the carbon atom into the epoxide to form a reactive lactone (a precursor to polyesters), while the reaction of the same epoxide with CO₂ results into a stable cyclic carbonate (Figure 1).

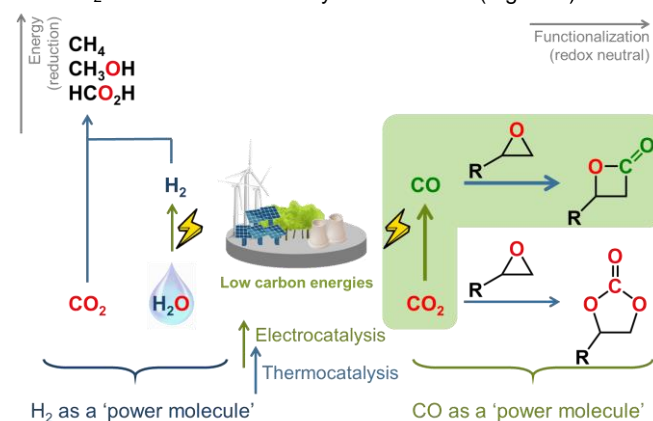


Figure 1. Integration of CO as a 'power molecule' for the formation of value-added chemicals from CO₂ by coupling electrocatalytic reduction with thermocatalytic functionalization.

CO₂ electroreduction to CO is indeed a well-established process, which has led to systems that operate with rate and selectivity close to the requirements for industrial usage.^[4] The first and unique illustration of such an integrated two-reaction process (CO₂ electroconversion to CO and carbonylation) was provided in 2017 by Skrydstrup *et al.*, who reported the preparation of pharmaceuticals through a palladium-catalysed carbonylative cross-coupling reaction.^[5] A related approach was exploited for the synthesis of ¹³C-labelled amides using ¹³CO₂ as a carbon source, however via CO₂ photoreduction and not electroreduction.^[6] In fact, these achievements were possible because the carbonylation steps proceed with sub-atmospheric partial pressures of CO and use noble-metal-based catalysts that are stable in the presence of air and moisture. In contrast, in most industrially relevant processes, CO, which is derived from fossil feedstocks (e.g. steam reforming of methane or autothermal reforming), has to be in the form of a pure stream or as a syngas and the catalytic reactions require high partial pressures of CO and are highly sensitive to air and moisture. This is true for the

production of chemicals such as acetic acid derivatives (Cativa and Eastman-Kodak processes, 12 Mt/yr), of large volume commodities (hydroformylation or oxo-process, 10 Mt/yr), as well as for Fisher-Tropsch synthesis of liquid fuels.^[7] Thus, coupling CO₂ electroreduction to CO and the thermocatalytic conversion of CO *via* such industrially significant carbonylation reactions faces a number of specific challenges that are yet to be addressed. First, electrolyzers have rarely been designed to generate high pressures of CO at the cathode.^[8] Second, no effort has been made to minimize production of side products (e.g. H₂, HCO₂H, etc.), or water and oxygen from the CO stream, to make it compatible with sensitive carbonylation catalysts. Third, new technological devices must be elaborated in order to allow direct coupling of the electrolyzer to the thermocatalytic reactor. On the other hand, efficient and stable solid materials, able to catalyze CO₂ conversion to CO with high current density and selectivity, are already available. Specifically, electrocatalysts based on Zn,^[9] Au^[10] and Ag^[11] are highly selective for the production of CO, with very little production of CH₄, H₂, formate and multi-carbon products.^[12] Recently reported electrocatalysts have been able to operate at ~ 90% Faradaic efficiency (FE) at rates greater than – 100 mA.cm⁻² by locally increasing the concentration of CO₂ using high pressures,^[8d] gas diffusion electrodes^[11, 13] or both.^[8a] Here we illustrate the potential of this strategy by combining: (i) an electrolytic cell, using a ZnAg alloy that we previously reported as a CO-selective cathodic catalytic material,^[8d] designed to generate a high pressure of CO; (ii) a purification system for removing inactivating pollutants; (iii) a reactor in which a cobalt-catalysed carbonylation of propylene oxide requiring a high CO pressure yields β-butyrolactone, with an excellent conversion of 80 %. Such lactones are key monomers for biodegradable

polyesters or precursors of polyurethanes and this is the first report of a lactone synthesis using CO₂ as a carbon source.^[14]

Results

Electrochemical reduction of CO₂ under pressure

Hierarchically porous AgZn alloy material was selected here for its excellent activity and selectivity for CO production.^[8d] Doping Zn with Ag in particular allows growing Zn dendrites thus resulting into a catalyst with high electrochemical surface area.^[8d] The production of the Ag-doped Zn electrocatalyst (with 9.4% Ag), using a Zn foil as the support, was undertaken through a co-electrodeposition procedure, leading to dendritic surfaces with a high electrochemical surface area, as reported previously.^[8d] As shown by scanning electron microscopy (SEM) and X-ray energy-dispersive spectroscopy (XEDS), the material had the same morphology (Figure S1) as previously obtained.^[8d] The electrode was used as the cathode in a single-compartment high-pressure autoclave adapted for electrocatalysis (see ESI for more information on the devices used in this study). A controlled current density of – 0.2 A.cm⁻² was applied over 8 hours at a CO₂ pressure of 8 bar in 0.1 M CsHCO₃, in order to evaluate the activity and stability of the catalyst. Larger current densities were avoided as they resulted into lower selectivity for CO₂ reduction and with an applied current density of – 0.2 A.cm⁻², a pressure over 6 bar was requested in order to limit H₂ production. Furthermore, CsHCO₃ was used here as the electrolyte as it was previously shown to optimize current density and selectivity, as compared to KHCO₃.^[15]

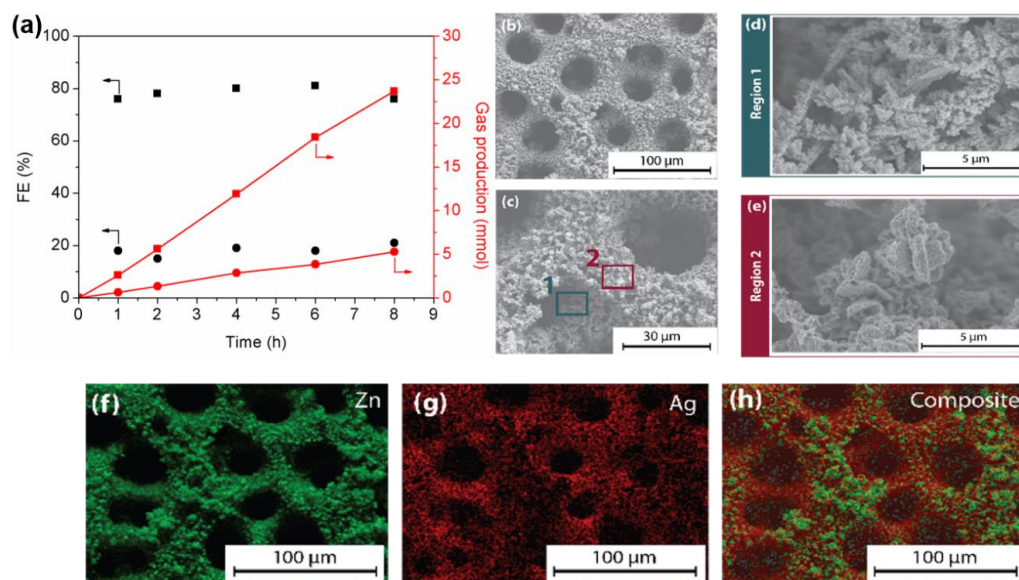


Figure 2. (a) Constant-current (–0.2 A.cm⁻²) electrolysis using a 9.4 %-Ag-doped Zn electrode in 0.1 M CsHCO₃ under 8 bar CO₂. Faradaic efficiencies (left axis: CO-black square and H₂-black circle) and gases production (right axis: CO-red square and H₂-red circle) for CO and H₂ are displayed. (b) and (c) SEM images of the Ag-doped Zn electrodes after 8 hours of electrolysis. (d) and (e) SEM images of the regions 1 and 2, respectively, indicated in (b) and (c), showing the dendritic Ag-doped Zn region in (d) and redeposited, pure Zn region in (e). (f), (g) and (h) XEDS analysis of the Ag-doped Zn surface after electrolysis, showing the presence of redeposited Zn on the topmost surface of the electrode.

Figure 2a reports both the amount of gaseous products within the headspace of the cell (right axis) and faradaic efficiencies (FE) for CO and H₂ (left axis) as a function of time. As shown in Figure 2a,

a stable FE for CO production was obtained, at around 80 %, while H₂ yield remained below 20 %. H₂ is an unavoidable by-product of the electrolysis since CO₂ electroreduction in aqueous

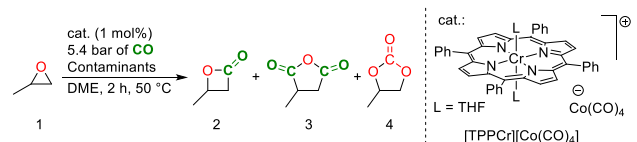
electrolytes occurs at potentials cathodic enough for driving proton reduction as well. Interestingly, this selectivity was not affected by the increased CO partial pressure (up to ca. 3 bar), thus excluding any poisoning of the catalyst surface, and CO₂ from the headspace continuously diffuses to the electrolyte (Figure S2). The tolerance of the catalyst to high CO partial pressures was assigned to the energetics of the key M–CO* intermediate (CO* represents CO adsorbed at the surface of the catalyst).^[16] Both Ag and Zn atoms have near zero ΔE for M–CO* bonds, which ensures release of the product out of the catalyst surface.

Post-electrolysis analysis of the catalyst surface was carried out by SEM (Figures 1b-e). While the original dendritic structure of the catalyst surface (Figure S1) remained intact after electrolysis (Figure 2d, marked Region 1 in Figure 2c), SEM images also clearly showed the presence of newly formed platelet structures (Figure 2e, marked Region 2 in Figure 2c). XEDS revealed that Region 1 contains the actual Ag/Zn alloy (Figure 2g and 2h), however with an increase of the Ag content from ~ 5 to ~ 10% (Figure S3), while at the topmost region (Region 2), pure Zn species were observed (Figure 2f and 2h and Figure S3). The latter are likely to derive from dissolution/redeposition of Zn at the surface of the alloy during catalysis. Nevertheless, this modification has no effect on the performances of the catalysts as shown by the stable current density and faradaic yields observed after 8 h reaction (Figure 2a).

Tolerance of carbonylation reactions towards contaminants

To ensure that the carbonylation reaction can proceed efficiently when coupled to the CO-generating electrolytic system described above, it was studied in the presence of various gas mixtures, aimed at emulating the outlet streams from the CO₂ electrolyser; namely, CO mixed with CO₂, H₂, H₂O (vapour) and O₂. The Cr/Co bimetallic complex [(TPP)Cr][Co(CO)₄] was selected as the catalyst, as it was designed by Coates *et al.* to promote the carbonylation of epoxides under mild pressures of CO (< 15 bar).^[17] While other epoxides are potential substrates for that reaction, propylene oxide was chosen because it is the main liquid epoxide produced in the petrochemistry. Standard tests were carried out with 1 mmol of propylene oxide as the substrate, 1 mol % of catalyst and 1 mL of solvent (dimethoxyethane, DME) under an initial partial pressure of 5.4 bar of CO for 2 hours. Under the standard conditions, epoxide (**1**) conversion was quantitative and lactone (**2**) was found to be the major product, together with minor quantities of commonly observed side products (acetone and oligomers) and methyl succinic anhydride (**3**), the latter compound deriving from carbonylation of the lactone product itself. The lactone (**2**) production yield in the presence of various gas mixtures is shown in Table 1.

Table 1. Conversion of propylene oxide (**1**) and yields of reaction products (**2**) and (**3**) during carbonylation using [(TPP)Cr][Co(CO)₄] as the catalyst under various gas mixtures representative of electrolysis gas streams^[a].



Entry	Composition of gas mixture (%)	Total pressure (bar)	Lactone yield (2, %)	Anhydride yield (3, %)	Carbonate yield (4, %)	Epoxide conversion (1, %)
1	CO (100)	5.4	77	3	0	>99
2	CO (80) H ₂ (20)	6	72	3	0	98
3	CO (80) CO ₂ (20)	6	87	0	0	98
4 ^[b]	CO ₂ (100)	45	0	0	0	35
5	CO (45) CO ₂ (45) H ₂ (10)	12	81	4	0	98
6	CO (95) O ₂ (5)	5.4	0	0	0	0
7	CO (100) H ₂ O (traces)	5.4	0	0	0	0

^[a] Reaction conditions: 1 mmol propylene oxide (**1**) in 1 mL of DME, in an autoclave charged with a partial pressure of 5.4 bar of CO. The autoclave was then heated for 2 h at 50 °C, then cooled down to 0 °C, depressurized, and the reaction mixture was analysed by ¹H NMR spectroscopy. A margin of error of 5 % is to be considered for all values (CO pressure, yields, conversion). The rest of the products mostly consists of acetone and a mixture of oligomers and polymers (See ESI for details and Table S1). ^[b] No CO was added

Coupling the electrochemical cell to the carbonylation reactor

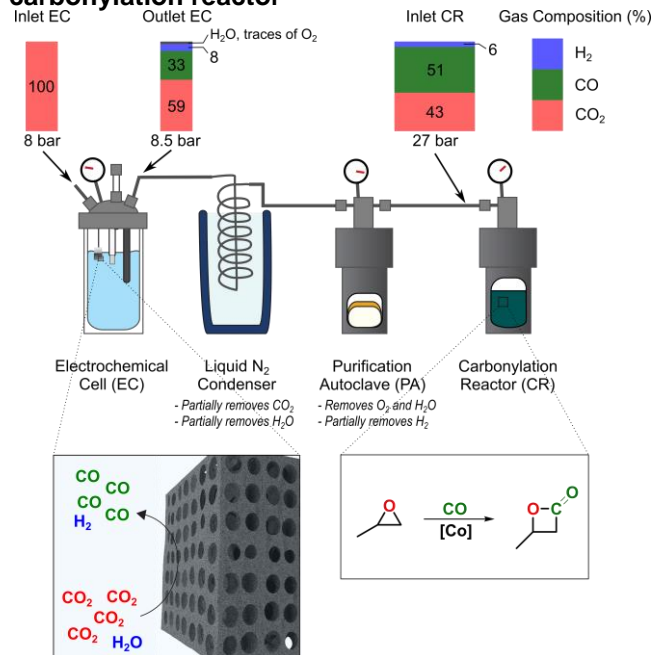
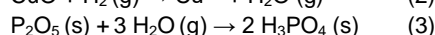
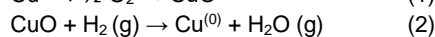


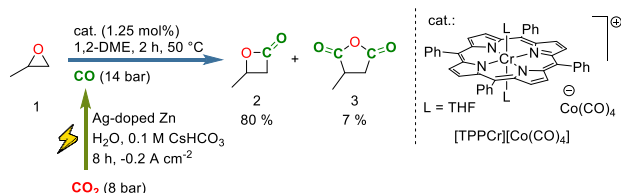
Figure 3. The linear technical set-up coupling the electrochemical cell to the carbonylation reactor *via* gas purification systems

After 8 h of electrolysis at -0.2 A.cm^{-2} under an initial CO_2 pressure of 8 bar, the gas mixture in the headspace of the electrolyser was composed of 33 % CO , 8 % H_2 and 59 % CO_2 , corresponding to a CO_2 conversion yield of 35 %, together with H_2O and traces of O_2 (estimated to less than 0.5 %), and the pressure was slightly increased to 8.5 bar. This increase was due to the production of H_2 as well as to the lower solubility of CO with respect to CO_2 . One should note that higher conversion could be achieved by prolonged electrolysis since the system is fully functional after 8h reaction (Figure 2a).

Given the high sensitivity of the carbonylation catalyst to water and oxygen, a device was designed to purify the gas mixture coming out from the electrochemical cell (EC) before transferring it to the carbonylation reactor (CR) (Figure 3 and Figures S4-S6). First, a liquid N_2 condenser (6 mL) was connected to the headspace of the EC in order to directly collect the gas mixture (140 mL), to increase its total pressure, and to liquefy most of the gaseous H_2O that thus remained in the condenser. The resulting partially purified gas mixture was then expanded into the purification system, consisting of an autoclave (17 mL) operating at 70°C , containing a desiccant (molecular sieves 4 \AA), a dehydrating agent (P_2O_5) and a catalyst for deoxygenation (typically metallic Cu on carbon, a material generally used as a glovebox purifier) to remove O_2 and residual H_2O . Since the gases were transferred into an autoclave of much smaller volume compared to the EC, the total pressure increased to 49 bar, with a partial pressure of CO of ca. 25 bar. Note that, in this setup, $\text{Cu}^{(0)}$ catalyzes the reduction of O_2 by H_2 (produced in the EC and present in the gas mixture) into water, according to Equations 1 and 2. The as-generated H_2O , along with any additional H_2O coming from the EC, was then removed according to Equation (3). A GC analysis of the reaction mixture after the purification system confirmed that O_2 and water were fully removed and that the gas mixture was composed of 51 % CO , 43 % CO_2 and 6 % H_2 .



The purified gas mixture was expanded into the CR, and a repressurization with argon allowed to transfer 57 % of the gas mixture (See Supplemental Information), leading to a partial pressure of CO of ca. 14 bar in the CR before carbonylation. The remaining CO can be also used in a second carbonylation reaction.



Scheme 1. Carbonylation of propylene oxide (**1**) with carbon monoxide produced from CO_2 electroreduction.

The CR contained 0.8 mmol of propylene oxide (**1**), 1.25 mol % of $[\text{TPPCr}][\text{Co}(\text{CO})_4]$ and 1 mL of 1,2-DME under an inert atmosphere of argon. The temperature of the reactor was set at 50°C and the carbonylation reaction started. After 2 hours, the reactor was cooled down in an ice bath to condense any volatile compound, depressurized and the liquids were collected, filtered over Celite, and analysed by $^1\text{H NMR}$ in CDCl_3 . We observed that

the epoxide (**1**) was fully converted into a mixture of products composed at 80 % of lactone (**2**), together with 7 % methyl succinic anhydride (**3**) and 9 % of acetone: this equated to 0.8 mmol of CO obtained from CO_2 incorporated in the carbonylation products. Overall, while 35 % of CO_2 was converted to CO in the electrochemical cell, 9 % of the injected CO was converted to lactone **2** and anhydride **3** in the carbonylation reactor, so that a yield of 1.7 % was measured from CO_2 to **2** and **3** (See ESI for calculation details). Although modest, this yield is a unique example of coupling CO_2 electroreduction with a thermocatalytic conversion of high pressure CO . It should hence be seen as a benchmark value for future progresses, highlighting the challenges in the field, which mainly concern developing energy efficient gas purification and recycling processes.

Discussion

To replace fossil resources in the industrial production of useful organic compounds and foster a circular economy, new sources of carbon are needed. A particularly appealing source of carbon is CO_2 as it is readily available (for example from waste industrial streams, where it is highly concentrated) and its consumption will limit greenhouse gas accumulation in the atmosphere. The chemical stability of CO_2 however restricts its transformation and the major industrialized conversion processes involving CO_2 are redox-neutral such as those leading to urea, salicylic acid, poly- or cyclic carbonates. To expand the scope of chemicals accessible from CO_2 , this carbon precursor should instead be simultaneously reduced and functionalized to exploit its carbon content into a useful product. This endeavour could be accomplished using carbon monoxide (CO) as a reactive intermediate and this 'power molecule' could be synthesized through CO_2 electroreduction before being further engaged in a carbonylation reaction (Figure 1).

Coupling the electrolytic reduction of CO_2 with a downstream use of CO first requires the production of a CO stream with a high Faradaic efficiency, to limit the quantity of side products, and high rates to enable the accumulation of large quantities of CO in the gas phase. In addition, carbonylation reactions relevant to industrial applications and the present carbonylation of epoxides necessitate CO pressures in the range 1-60 bar. Very few high-pressure electrocatalytic systems have been reported so far.^[8] In these systems, the high-pressure (from 3 to 50 bar) of CO_2 introduced in the cell was mainly aimed at removing the mass transport limitations associated with the low solubility of CO_2 in aqueous electrolytes to achieve high current densities. Therefore, no information was given regarding the final pressure of CO and no effort has been made to purify the gas product stream. Furthermore, the high selectivity of the reaction was obtained thanks to Ag-based electrodes in all cases. The original catalyst used in our study is instead mostly based on Zn, a non-noble abundant metal, doped with a small amount of Ag, and with such a cathode electrolysis could be run at 8 bar with high current density (-200 mA.cm^{-2}) and good selectivity for CO production. Most importantly, the partial pressure of CO was monitored throughout the process from the electrolyzer up to the carbonylation reactor where it could reach a value up to 14 bar after several purification steps.

As CO is generated from the co-electrolysis of CO_2 and water, the gas stream also presents various amounts of potential pollutants

and poisons for the carbonylation thermocatalyst [TPPCr][Co(CO)₄], namely unreacted CO₂, O₂, H₂, and H₂O. The tolerance of thermocatalysts towards common gas contaminants such as hydrogen and carbon dioxide is usually not considered in the development and characterization of such catalytic systems, which in turn leads to increased complexity upon integration in catalytic sequences. The catalytic results from Table 1 provide a number of interesting information. First, although epoxides and CO₂ are known to react to generate organic carbonates, [TPPCr][Co(CO)₄] is a selective carbonylation catalyst, exclusively converting propylene oxide and CO, and leaving CO₂ unreacted. Second, interestingly, this catalyst is not sensitive to CO₂ and H₂. Third, it is in contrast completely deactivated in the presence of water as well as of traces of O₂. Taking advantage of the production of small quantities of H₂ upon CO₂/H₂O co-electrolysis, it is nevertheless possible to reduce O₂ to water, using copper(0) as a solid catalyst (Figure 3). The reactivity of carbonylation catalysts towards oxygen and/or moisture is well established and, to this end, systems for oxygen and water removal from gaseous streams has been used routinely in the industry, that could be implemented in this system upon scaling-up.^[19] It is foreseeable that these technologies, such as cryogenic separation, pressure swing adsorption or membrane separation will be also useful when scaling-up tandem CO₂-electroreduction and carbonylation reactions. Using these techniques would allow a more efficient gas transfer and purification from the production of CO to its utilisation. This would have the benefit of avoiding the use of P₂O₅ as a sacrificial desiccant, as well as increase the total yield in carbon of the system almost two-fold (1.7 to 3 %). Recycling the CO after carbonylation would also allow for a yield increase approaching that of the electroreduction. To this end, several processes have already been described in patents by Novomer.^[20] Catalysts used for this carbonylation can also be recycled, as described by Novomer or Yoon (using supporting techniques).^[20-21] Besides this purification issue, obviously the overall process is energy-demanding and thus would be relevant only if it is fuelled with renewable energy.

Overall, the formation of lactone (**2**) from CO₂ and propylene oxide, using CO as an intermediate (Scheme 1), enables the formation of a useful cyclic ester. The reaction chemistry between CO₂ and epoxides is well documented for the formation of organic carbonates and utilized to produce polycarbonates, the only class of polymer where CO₂ is incorporated in the polymer chain.^[22] Industrial deployments are underway to commercialize these CO₂-derived carbonates.^[23] The addition of an electrolytic step unlocks for the first time the production of a monomer utilized in the production of polyesters, such as polyhydroxybutyrate or polysuccinate^[24]. Interestingly, while 43 wt% of the cyclic carbonate (**4**) derive from CO₂, this value reaches 33 wt% in lactone (**2**) thereby showing that a significant portion of the product is based on a renewable carbon source.

Beyond the formation of lactone (**2**), coupling the electroreduction of CO₂ to CO with a downstream reaction may prove of interest in several other carbonylation processes relying today on fossil sources of CO. The present work hence paves the way to improve the uptake of CO₂ in functional chemicals. Indeed, industrial carbonylation processes currently utilize low valent metal complexes as homogeneous catalysts to produce acetic acid,^[7a] phosgene^[25] or dimethylformamide^[26] from 9.6 Mt/yr of CO worldwide. The production of such compounds from CO₂ would then involve ca. 15 Mt of CO₂. Other chemicals, such as

methanol^[27] and butanal,^[28] also utilize CO, but as a syngas. These syngas-based routes represent a large consumption of 45 Mt_{CO}/yr. The implementation of CO₂ and H₂O co-electrolysis for syngas production and further conversion to methanol or butanal production offers a potential mitigation of ca. 70 Mt/yr of CO₂.

Conclusion

Useful monomers were synthesized from CO₂ by coupling an electrocatalytic reduction and a thermocatalytic carbonylation reaction. The use of an Ag-doped Zn alloy ensured efficient and stable generation of CO to very high conversions. Such a CO stream also contains pollutants such as H₂O, O₂, H₂ and CO₂, which can be detrimental to the carbonylation catalyst. The latter was found to be tolerant to H₂ and CO₂, but not to H₂O and O₂ which were removed using a gas purification system. The coupled electrocatalytic cell / carbonylation reactor system could then be used to generate β -butyrolactone with a yield of 80 % from propylene oxide, under a partial pressure of CO of ca. 14 bar, produced from CO₂.

These results represent the first example of high-pressure carbonylation chemistry undertaken from CO₂-derived CO, which will be key to undertaking sustainable organic reactions. Future work should focus on the development of new carbonylation catalysts which are robust towards usual contaminants from CO₂ electroreduction for a faster and more efficient coupling of electrocatalysis and thermocatalysis. Furthermore, this work paves the ways to other useful carbonylation processes relevant in industrial set-ups.

Experimental Section

Electrode preparation. Electrodes were prepared on 1 cm² Zn foil first polished by P1200 and P2400 emery paper, successively, then treated by sonication in water before deposition. Each electrode was then immersed in a 1.5 M H₂SO₄ aqueous solution of 0.01 M AgNO₃ and 0.19 M ZnSO₄ and exposed to - 4 A.cm⁻² for 30 s using a three-electrode set-up with an Ag/AgCl (KCl sat.) reference and Pt counter electrode. In each case, the electrode was immediately rinsed with milliQ water and air-dried.

Electrocatalytic CO₂ reduction. High-pressure CO₂ reduction experiments were carried out in a custom-made single-compartment high-pressure cell (EC) using a Ag/AgCl reference (3 M KCl) and graphite counter electrode. Each experiment was carried out in 215 mL of electrolyte, which was degassed with CO₂ prior to the electrolysis. The pressurised vessel was left standing for one hour to saturate the solution before electrolysis and then controlled current densities were applied across the cathode and anode for 8 h.

Purification. Purification was carried out in a high pressure autoclave, designed and built at CEA. The purification autoclave (PA) was filled under atmospheric conditions with a glass tube. This tube was filled with a layer of 1 cm of P₂O₅, followed by a thin layer of molecular sieves, copper on carbon cylinder and molecular sieves on the top. A liquid N₂ condenser was then connected between the electrocatalytic cell and the PA. The system was immediately purged three times with 10 bar of Ar. After being brought back to atmospheric pressure, gases from the

EC were condensed with liquid N₂, then allowed to expand to the PA upon thawing back to room temperature. The PA was closed and left for 20 hours at 70 °C.

Carbonylation. Under an argon atmosphere, a 1 mL vial was filled with 70 µL of propylene oxide, 1 mL of 1,2-dimethoxyethane and 8.3 mg of [TPPCr][Co(CO)₄]. This mixture was transferred with a syringe to a carbonylation reactor (CR), immediately purged three times with 10 bar of argon. It was then connected to the PA, gases from the PA were expanded into the CR. The CR was closed, and heated to 50 °C for 2 h with stirring. The CR was then cooled down to 0 °C and carefully opened to release the pressure. A 500 µL aliquot of the final reaction mixture was sampled, to which CDCl₃ and mesitylene (internal standard) were added. The resulting solution was filtered on a Celite pad, and analysed by ¹H NMR spectroscopy.

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Keywords: electrochemistry • homogeneous catalysis • carbonylation • CO • CO₂

- [1] J. Artz, T. E. Müller, K. Thenert, J. Kleinekorde, R. Meys, A. Sternberg, A. Bardow, W. Leitner, *Chem. Rev.* **2018**, *118*, 434-504.
- [2] C. Das Neves Gomes, O. Jacquet, C. Villiers, P. Thuéry, M. Ephritikhine, T. Cantat, *Angew. Chem. Int. Ed.* **2012**, *51*, 187-190; *Angew. Chem.* **2012**, *124*, 191-194.
- [3] D. U. Nielsen, X.-M. Hu, K. Daasbjerg, T. Skrydstrup, *Nature Catal.* **2018**, *1*, 244-254.
- [4] a) O. S. Bushuyev, P. De Luna, C. T. Dinh, L. Tao, G. Saur, J. van de Lagemaat, S. O. Kelley, E. H. Sargent, *Joule* **2018**, *2*, 825-832; b) P. De Luna, C. Hahn, D. Higgins, S. A. Jaffer, T. F. Jaramillo, E. H. Sargent, *Science* **2019**, *364*, eaav3506; c) F. P. García de Arquer, C.-T. Dinh, A. Ozden, J. Wicks, C. McCallum, A. R. Kirmani, D.-H. Nam, C. Gabardo, A. Seifitokaldani, X. Wang, Y. C. Li, F. Li, J. Edwards, L. J. Richter, S. J. Thorpe, D. Sinton, E. H. Sargent, *Science* **2020**, *367*, 661; d) X. Wang, Z. Wang, F. P. García de Arquer, C.-T. Dinh, A. Ozden, Y. C. Li, D.-H. Nam, J. Li, Y.-S. Liu, J. Wicks, Z. Chen, M. Chi, B. Chen, Y. Wang, J. Tam, J. Y. Howe, A. Proppe, P. Todorović, F. Li, T.-T. Zhuang, C. M. Gabardo, A. R. Kirmani, C. McCallum, S.-F. Hung, Y. Lum, M. Luo, Y. Min, A. Xu, C. P. O'Brien, B. Stephen, B. Sun, A. H. Ip, L. J. Richter, S. O. Kelley, D. Sinton, E. H. Sargent, *Nature Energy* **2020**, *5*, 478-486.
- [5] M. T. Jensen, M. H. Rønne, A. K. Ravn, R. W. Juhl, D. U. Nielsen, X.-M. Hu, S. U. Pedersen, K. Daasbjerg, T. Skrydstrup, *Nature Commun.* **2017**, *8*, 489.
- [6] P. Gotico, A. Del Vecchio, D. Audisio, A. Quaranta, Z. Halime, W. Leibl, A. Aukauloo, *ChemPhotoChem* **2018**, *2*, 715-719.
- [7] a) C. Le Berre, P. Serp, P. Kalck, G. P. Torrence, *Ullmann's Encyclopedia of Industrial Chemistry* **2014**, 1-34; b) A. Börner, R. Franke, *Hydroformylation : fundamentals, processes, and applications in organic synthesis*, Wiley-VCH, **2016**.
- [8] a) E. J. Dufek, T. E. Lister, S. G. Stone, M. E. Mcllwain, *J. Electrochem. Soc.* **2012**, *159*, F514-F517; b) C. M. Gabardo, A. Seifitokaldani, J. P. Edwards, C.-T. Dinh, T. Burdyny, M. G. Kibria, C. P. O'Brien, E. H. Sargent, D. Sinton, *Energy & Environmental Science* **2018**, *11*, 2531-2539; c) B. Endrödi, E. Kecsenovity, A. Samu, F. Darvas, R. V. Jones, V. Török, A. Danyi, C. Janáky, *ACS Energy Letters* **2019**, *4*, 1770-1777; d) S. Lamaison, D. Wakerley, J. Blanchard, D. Montero, G. Rousse, D. Mercier, P. Marcus, D. Taverna, D. Giaume, V. Mougél, M. Fontecave, *Joule* **2020**, *4*, 395-406; e) J. P. Edwards, Y. Xu, C. M. Gabardo, C.-T. Dinh, J. Li, Z. Qi, A. Ozden, E. H. Sargent, D. Sinton, *Applied Energy* **2020**, *261*, 114305.
- [9] D. H. Won, H. Shin, J. Koh, J. Chung, H. S. Lee, H. Kim, S. I. Woo, *Angew. Chem. Int. Ed.* **2016**, *55*, 9297-9300; *Angew. Chem.* **2016**, *128*, 9443-9446.
- [10] A. Wuttig, M. Yaguchi, K. Motobayashi, M. Osawa, Y. Surendranath, *Proceedings of the National Academy of Sciences* **2016**, *113*, E4585.
- [11] S. Ma, R. Luo, J. I. Gold, A. Z. Yu, B. Kim, P. J. A. Kenis, *Journal of Materials Chemistry A* **2016**, *4*, 8573-8578.
- [12] R. Küngas, *J. Electrochem. Soc.* **2020**, *167*, 044508.
- [13] a) S. Malkhandi, B. S. Yeo, *Current Opinion in Chemical Engineering* **2019**, *26*, 112-121; b) D. Higgins, C. Hahn, C. Xiang, T. F. Jaramillo, A. Z. Weber, *ACS Energy Letters* **2019**, *4*, 317-324.
- [14] E. Gubbels, T. Heitz, M. Yamamoto, V. Chilekar, S. Zorbakhsh, M. Gepreags, H. Köpnick, M. Schmidt, W. Brüggling, J. Rüter, W. Kaminsky, *Ullmann's Encyclopedia of Industrial Chemistry* **2018**, 1-30.
- [15] a) D. Karapinar, N. T. Huan, N. Ranjbar Sahraie, J. Li, D. Wakerley, N. Touati, S. Zanna, D. Taverna, L. H. Galvão Tizei, A. Zitolo, F. Jaouen, V. Mougél, M. Fontecave, *Angew. Chem. Int. Ed.* **2019**, *58*, 15098-15103; *Angew. Chem.* **2016**, *131* 15242-15247; b) M. R. Singh, Y. Kwon, Y. Lum, J. W. Ager, A. T. Bell, *J. Am. Chem. Soc.* **2016**, *138*, 13006-13012.
- [16] A. Bagger, W. Ju, A. S. Varela, P. Strasser, J. Rossmeisl, *ChemPhysChem* **2017**, *18*, 3266-3273.
- [17] a) J. A. R. Schmidt, V. Mahadevan, Y. D. Y. L. Getzler, G. W. Coates, *Org. Lett.* **2004**, *6*, 373-376; b) J. W. Kramer, E. B. Lobkovsky, G. W. Coates, *Org. Lett.* **2006**, *8*, 3709-3712.
- [18] H. Büttner, L. Longwitz, J. Steinbauer, C. Wulf, T. Werner, *Top. Curr. Chem.* **2017**, *375*, 50.
- [19] S. J. Cooke, in *Kent and Riegel's Handbook of Industrial Chemistry and Biotechnology* (Ed.: J. A. Kent), Springer US, Boston, MA, **2007**, pp. 1215-1233.
- [20] S. D. Allen, R. R. Valente, H. Lee, A. E. Cherian, D. L. Bunning, N. A. Clinton, O. S. Fruchey, B. D. Dombek, Novomer, Inc., **2016**.
- [21] J. Jiang, S. Yoon, *Scientific Reports* **2018**, *8*, 13243.
- [22] S. Liu, X. Wang, *Current Opinion in Green and Sustainable Chemistry* **2017**, *3*, 61-66.
- [23] a) R. Chauvy, G. De Weireld, *Energy Technology* **2020**, *n/a*, 2000627; b) S. A. Stevenson, *AIChE J.* **2019**, *65*, e16695.
- [24] A. Künkel, J. Becker, L. Börger, J. Hamprecht, S. Koltzenburg, R. Loos, M. B. Schick, K. Schlegel, C. Sinkel, G. Skupin, M. Yamamoto, *Ullmann's Encyclopedia of Industrial Chemistry* **2016**, 1-29.
- [25] L. Cotarca, C. Lange, K. Meurer, J. Pauluhn, *Ullmann's Encyclopedia of Industrial Chemistry* **2019**, 1-30.
- [26] H. Bipp, H. Kieczka, *Ullmann's Encyclopedia of Industrial Chemistry* **2011**.
- [27] J. Ott, V. Gronemann, F. Pontzen, E. Fiedler, G. Grossmann, D. B. Kersebohm, G. Weiss, C. Witte, *Ullmann's Encyclopedia of Industrial Chemistry* **2012**.
- [28] D. K. Raff, *Ullmann's Encyclopedia of Industrial Chemistry* **2013**.