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# Coupling electrocatalytic CO<sub>2</sub> reduction with thermocatalysis enables the formation of a lactone monomer

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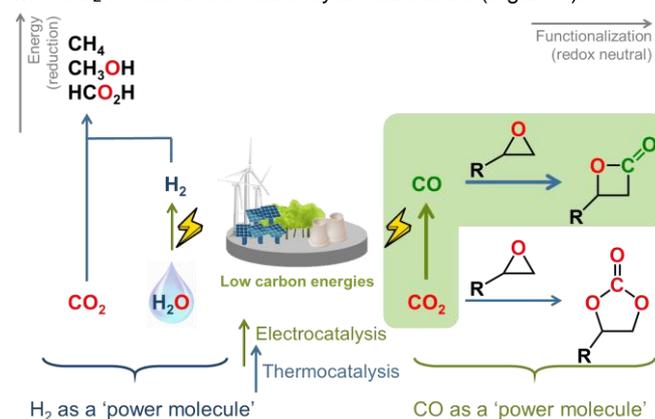
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**Abstract:** Carbonylation reactions that generate high-value chemical feedstocks are integral to the formation of many industrially significant compounds. However, these processes require the use of CO, which is invariably derived from fossil-fuel-reforming reactions. CO may also be generated through the electroreduction of CO<sub>2</sub>, but the coupling of these two processes is yet to be considered. Merging electrocatalytic reduction of CO<sub>2</sub> to CO with thermocatalytic use of CO would expand the range of the chemicals produced from CO<sub>2</sub>. This work describes for the first time the development of a system coupling a high-pressure CO<sub>2</sub> 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  $\beta$ -butyrolactone by thermal catalysis, the latter step having a reaction yield above 80%. While the production of monomers and polymers from CO<sub>2</sub> is currently limited to organic carbonates, this strategy opens up the access to lactones from CO<sub>2</sub>, 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 CO<sub>2</sub>, should be utilized as a carbon feedstock to replace petrochemicals.<sup>[1]</sup> Bulk and fine chemicals contain carbon atoms in a variety of oxidation states ranging from +IV (in CO<sub>2</sub> and carbonates) to -III (in alkyl chains). However current processes developed at scale in the industry rely on the functionalization of CO<sub>2</sub> 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 CO<sub>2</sub>, instead, requires the elaboration of transformation sequences able to couple the reduction of CO<sub>2</sub> with its functionalization, in a Power-To-X approach.<sup>[2]</sup> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub>.<sup>[3]</sup> Indeed, energizing CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> by coupling electrocatalytic reduction with thermocatalytic functionalization.

CO<sub>2</sub> 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.<sup>[4]</sup> The first and unique illustration of such an integrated two-reaction process (CO<sub>2</sub> 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.<sup>[5]</sup> A related approach was exploited for the synthesis of <sup>13</sup>C-labelled amides using <sup>13</sup>CO<sub>2</sub> as a carbon source, however via CO<sub>2</sub> photoreduction and not electroreduction.<sup>[6]</sup> 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

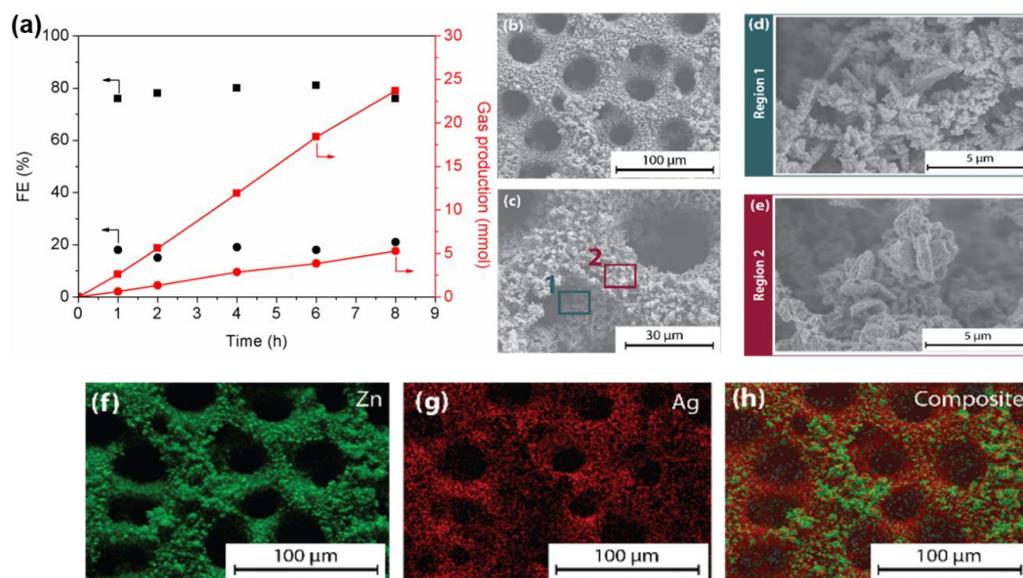
production of chemicals such as acetic acid derivatives (Cativa and Eastman-Kodak processes, 12 Mt/yr), of large volume commodities (hydroformylation or oxo-process, 10 Mt/yr), as well as for Fisher-Tropsch synthesis of liquid fuels.<sup>[7]</sup> Thus, coupling CO<sub>2</sub> electroreduction to CO 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.<sup>[8]</sup> Second, no effort has been made to minimize production of side products (e.g. H<sub>2</sub>, HCO<sub>2</sub>H, 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 CO<sub>2</sub> conversion to CO with high current density and selectivity, are already available. Specifically, electrocatalysts based on Zn,<sup>[9]</sup> Au<sup>[10]</sup> and Ag<sup>[11]</sup> are highly selective for the production of CO, with very little production of CH<sub>4</sub>, H<sub>2</sub>, formate and multi-carbon products.<sup>[12]</sup> Recently reported electrocatalysts have been able to operate at ~ 90% Faradaic efficiency (FE) at rates greater than – 100 mA.cm<sup>-2</sup> by locally increasing the concentration of CO<sub>2</sub> using high pressures,<sup>[8d]</sup> gas diffusion electrodes<sup>[11, 13]</sup> or both.<sup>[8a]</sup> 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,<sup>[8d]</sup> 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 CO<sub>2</sub> as a carbon source.<sup>[14]</sup>

## Results

### Electrochemical reduction of CO<sub>2</sub> under pressure

Hierarchically porous AgZn alloy material was selected here for its excellent activity and selectivity for CO production.<sup>[8d]</sup> Doping Zn with Ag in particular allows growing Zn dendrites thus resulting into a catalyst with high electrochemical surface area.<sup>[8d]</sup> 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.<sup>[8d]</sup> 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.<sup>[8d]</sup> 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<sup>-2</sup> was applied over 8 hours at a CO<sub>2</sub> pressure of 8 bar in 0.1 M CsHCO<sub>3</sub>, in order to evaluate the activity and stability of the catalyst. Larger current densities were avoided as they resulted into lower selectivity for CO<sub>2</sub> reduction and with an applied current density of – 0.2 A.cm<sup>-2</sup>, a pressure over 6 bar was requested in order to limit H<sub>2</sub> production. Furthermore, CsHCO<sub>3</sub> was used here as the electrolyte as it was previously shown to optimize current density and selectivity, as compared to KHCO<sub>3</sub>.<sup>[15]</sup>



**Figure 2.** (a) Constant-current (–0.2 A.cm<sup>-2</sup>) electrolysis using a 9.4 %-Ag-doped Zn electrode in 0.1 M CsHCO<sub>3</sub> under 8 bar CO<sub>2</sub>. Faradaic efficiencies (left axis: CO-black square and H<sub>2</sub>-black circle) and gases production (right axis: CO-red square and H<sub>2</sub>-red circle) for CO and H<sub>2</sub> 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 H<sub>2</sub> (left axis) as a function of time. As shown in Figure 2a,

a stable FE for CO production was obtained, at around 80%, while H<sub>2</sub> yield remained below 20%. H<sub>2</sub> is an unavoidable by-product of the electrolysis since CO<sub>2</sub> electroreduction in aqueous

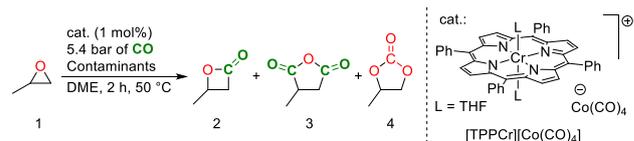
electrolytes occurs at potentials cathodic enough for driving proton reduction as well. Interestingly, this selectivity was not affected by the increased CO partial pressure (up to ca. 3 bar), thus excluding any poisoning of the catalyst surface, and CO<sub>2</sub> from the headspace continuously diffuses 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).<sup>[16]</sup> 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 CO<sub>2</sub> electrolyser; namely, CO mixed with CO<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O (vapour) and O<sub>2</sub>. The Cr/Co bimetallic complex [(TPP)Cr][Co(CO)<sub>4</sub>] 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).<sup>[17]</sup> 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.

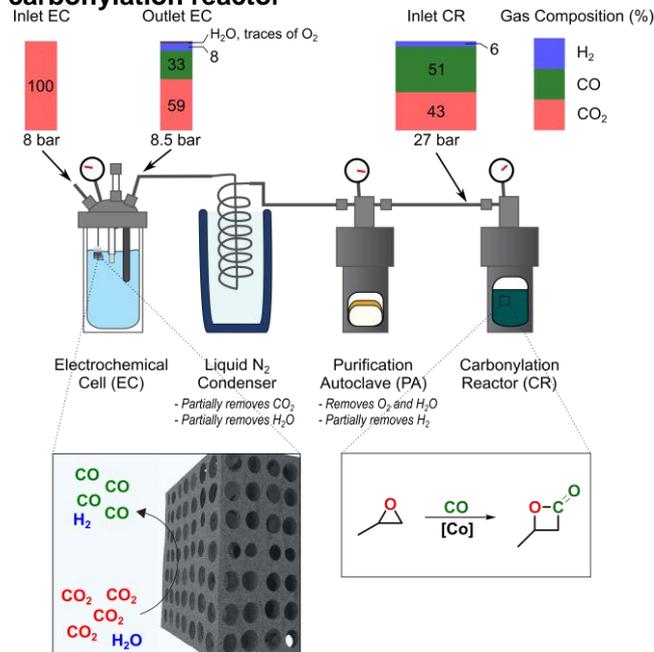
**Table 1.** Conversion of propylene oxide (**1**) and yields of reaction products (**2**) and (**3**) during carbonylation using [(TPP)Cr][Co(CO)<sub>4</sub>] as the catalyst under various gas mixtures representative of electrolysis gas streams<sup>[a]</sup>.



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 <sub>2</sub> (20)	6	72	3	0	98
3	CO (80) CO <sub>2</sub> (20)	6	87	0	0	98
4 <sup>[b]</sup>	CO <sub>2</sub> (100)	45	0	0	0	35
5	CO (45) CO <sub>2</sub> (45) H <sub>2</sub> (10)	12	81	4	0	98
6	CO (95) O <sub>2</sub> (5)	5.4	0	0	0	0
7	CO (100) H <sub>2</sub> O (traces)	5.4	0	0	0	0

<sup>[a]</sup> 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 <sup>1</sup>H 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). <sup>[b]</sup> No CO was added

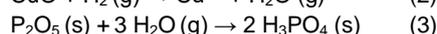
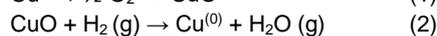
### Coupling the electrochemical cell to the carbonylation reactor



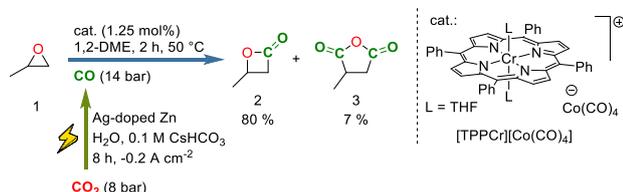
**Figure 3.** The linear technical set-up coupling the electrochemical cell to the carbonylation reactor via gas purification systems

After 8 h of electrolysis at  $-0.2 \text{ A.cm}^{-2}$  under an initial  $\text{CO}_2$  pressure of 8 bar, the gas mixture in the headspace of the electrolyser was composed of 33 %  $\text{CO}$ , 8 %  $\text{H}_2$  and 59 %  $\text{CO}_2$ , corresponding to a  $\text{CO}_2$  conversion yield of 35 %, together with  $\text{H}_2\text{O}$  and traces of  $\text{O}_2$  (estimated to less than 0.5 %), and the pressure was slightly increased to 8.5 bar. This increase was due to the production of  $\text{H}_2$  as well as to the lower solubility of  $\text{CO}$  with respect to  $\text{CO}_2$ . 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  $\text{N}_2$  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  $\text{H}_2\text{O}$  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  $70^\circ\text{C}$ , containing a desiccant (molecular sieves  $4 \text{ \AA}$ ), a dehydrating agent ( $\text{P}_2\text{O}_5$ ) and a catalyst for deoxygenation (typically metallic  $\text{Cu}$  on carbon, a material generally used as a glovebox purifier) to remove  $\text{O}_2$  and residual  $\text{H}_2\text{O}$ . 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  $\text{CO}$  of ca. 25 bar. Note that, in this setup,  $\text{Cu}^{(0)}$  catalyzes the reduction of  $\text{O}_2$  by  $\text{H}_2$  (produced in the EC and present in the gas mixture) into water, according to Equations 1 and 2. The as-generated  $\text{H}_2\text{O}$ , along with any additional  $\text{H}_2\text{O}$  coming from the EC, was then removed according to Equation (3). A GC analysis of the reaction mixture after the purification system confirmed that  $\text{O}_2$  and water were fully removed and that the gas mixture was composed of 51 %  $\text{CO}$ , 43 %  $\text{CO}_2$  and 6 %  $\text{H}_2$ .



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  $\text{CO}$  of ca. 14 bar in the CR before carbonylation. The remaining  $\text{CO}$  can be also used in a second carbonylation reaction.



**Scheme 1.** Carbonylation of propylene oxide (**1**) with carbon monoxide produced from  $\text{CO}_2$  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  $50^\circ\text{C}$  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  $\text{CDCl}_3$ . 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  $\text{CO}$  obtained from  $\text{CO}_2$  incorporated in the carbonylation products. Overall, while 35 % of  $\text{CO}_2$  was converted to  $\text{CO}$  in the electrochemical cell, 9 % of the injected  $\text{CO}$  was converted to lactone **2** and anhydride **3** in the carbonylation reactor, so that a yield of 1.7 % was measured from  $\text{CO}_2$  to **2** and **3** (See ESI for calculation details). Although modest, this yield is a unique example of coupling  $\text{CO}_2$  electroreduction with a thermocatalytic conversion of high pressure  $\text{CO}$ . 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  $\text{CO}_2$  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  $\text{CO}_2$  however restricts its transformation and the major industrialized conversion processes involving  $\text{CO}_2$  are redox-neutral such as those leading to urea, salicylic acid, poly- or cyclic carbonates. To expand the scope of chemicals accessible from  $\text{CO}_2$ , 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 ( $\text{CO}$ ) as a reactive intermediate and this 'power molecule' could be synthesized through  $\text{CO}_2$  electroreduction before being further engaged in a carbonylation reaction (Figure 1).

Coupling the electrolytic reduction of  $\text{CO}_2$  with a downstream use of  $\text{CO}$  first requires the production of a  $\text{CO}$  stream with a high Faradaic efficiency, to limit the quantity of side products, and high rates to enable the accumulation of large quantities of  $\text{CO}$  in the gas phase. In addition, carbonylation reactions relevant to industrial applications and the present carbonylation of epoxides necessitate  $\text{CO}$  pressures in the range 1-60 bar. Very few high-pressure electrocatalytic systems have been reported so far.<sup>[8]</sup> In these systems, the high-pressure (from 3 to 50 bar) of  $\text{CO}_2$  introduced in the cell was mainly aimed at removing the mass transport limitations associated with the low solubility of  $\text{CO}_2$  in aqueous electrolytes to achieve high current densities. Therefore, no information was given regarding the final pressure of  $\text{CO}$  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 ( $-200 \text{ mA.cm}^{-2}$ ) and good selectivity for  $\text{CO}$  production. Most importantly, the partial pressure of  $\text{CO}$  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  $\text{CO}$  is generated from the co-electrolysis of  $\text{CO}_2$  and water, the gas stream also presents various amounts of potential pollutants

and poisons for the carbonylation thermocatalyst [TPPCr][Co(CO)<sub>4</sub>], namely unreacted CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>, and H<sub>2</sub>O. 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 CO<sub>2</sub> are known to react to generate organic carbonates, [TPPCr][Co(CO)<sub>4</sub>] is a selective carbonylation catalyst, exclusively converting propylene oxide and CO, and leaving CO<sub>2</sub> unreacted. Second, interestingly, this catalyst is not sensitive to CO<sub>2</sub> and H<sub>2</sub>. Third, it is in contrast completely deactivated in the presence of water as well as of traces of O<sub>2</sub>. Taking advantage of the production of small quantities of H<sub>2</sub> upon CO<sub>2</sub>/H<sub>2</sub>O co-electrolysis, it is nevertheless possible to reduce O<sub>2</sub> 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.<sup>[19]</sup> It is foreseeable that these technologies, such as cryogenic separation, pressure swing adsorption or membrane separation will be also useful when scaling-up tandem CO<sub>2</sub>-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 P<sub>2</sub>O<sub>5</sub> 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.<sup>[20]</sup> Catalysts used for this carbonylation can also be recycled, as described by Novomer or Yoon (using supporting techniques).<sup>[20-21]</sup> 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 CO<sub>2</sub> and propylene oxide, using CO as an intermediate (Scheme 1), enables the formation of a useful cyclic ester. The reaction chemistry between CO<sub>2</sub> and epoxides is well documented for the formation of organic carbonates and utilized to produce polycarbonates, the only class of polymer where CO<sub>2</sub> is incorporated in the polymer chain.<sup>[22]</sup> Industrial deployments are underway to commercialize these CO<sub>2</sub>-derived carbonates.<sup>[23]</sup> 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<sup>[24]</sup>. Interestingly, while 43 wt% of the cyclic carbonate (**4**) derive from CO<sub>2</sub>, 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 CO<sub>2</sub> 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 CO<sub>2</sub> in functional chemicals. Indeed, industrial carbonylation processes currently utilize low valent metal complexes as homogeneous catalysts to produce acetic acid,<sup>[7a]</sup> phosgene<sup>[25]</sup> or dimethylformamide<sup>[26]</sup> from 9.6 Mt/yr of CO worldwide. The production of such compounds from CO<sub>2</sub> would then involve ca. 15 Mt of CO<sub>2</sub>. Other chemicals, such as

methanol<sup>[27]</sup> and butanal,<sup>[28]</sup> also utilize CO, but as a syngas. These syngas-based routes represent a large consumption of 45 Mt<sub>CO</sub>/yr. The implementation of CO<sub>2</sub> and H<sub>2</sub>O co-electrolysis for syngas production and further conversion to methanol or butanal production offers a potential mitigation of ca. 70 Mt/yr of CO<sub>2</sub>.

## Conclusion

Useful monomers were synthesized from CO<sub>2</sub> 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 H<sub>2</sub>O, O<sub>2</sub>, H<sub>2</sub> and CO<sub>2</sub>, which can be detrimental to the carbonylation catalyst. The latter was found to be tolerant to H<sub>2</sub> and CO<sub>2</sub>, but not to H<sub>2</sub>O and O<sub>2</sub> 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 CO<sub>2</sub>.

These results represent the first example of high-pressure carbonylation chemistry undertaken from CO<sub>2</sub>-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 CO<sub>2</sub> 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 cm<sup>2</sup> 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 H<sub>2</sub>SO<sub>4</sub> aqueous solution of 0.01 M AgNO<sub>3</sub> and 0.19 M ZnSO<sub>4</sub> and exposed to – 4 A.cm<sup>-2</sup> 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 CO<sub>2</sub> reduction.** High-pressure CO<sub>2</sub> 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 CO<sub>2</sub> 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 P<sub>2</sub>O<sub>5</sub>, followed by a thin layer of molecular sieves, copper on carbon cylinder and molecular sieves on the top. A liquid N<sub>2</sub> 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 N<sub>2</sub>, 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)<sub>4</sub>]. 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 CDCl<sub>3</sub> and mesitylene (internal standard) were added. The resulting solution was filtered on a Celite pad, and analysed by <sup>1</sup>H NMR spectroscopy.

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