

Cite this: *Chem. Commun.*, 2011, **47**, 11888–11890

www.rsc.org/chemcomm

COMMUNICATION

# Electrosynthesis of cyclic carbonates from epoxides and atmospheric pressure carbon dioxide†

Benjamin R. Buckley,\* Anish P. Patel and K. G. Upul Wijayantha\*

Received 2nd September 2011, Accepted 22nd September 2011

DOI: 10.1039/c1cc15467b

**The use of CO<sub>2</sub> for the preparation of value-added compounds has dramatically increased due to increased global warming concerns. We herein report an electrochemical cell containing a copper cathode and a magnesium anode that effectively converts epoxides and carbon dioxide to cyclic carbonates under mild electrochemical conditions at atmospheric pressure.**

Carbon dioxide is arguably the main contributor to the increased concentration of gases within the atmosphere, in fact since the dawn of the industrial revolution CO<sub>2</sub> concentration within the atmosphere has annually increased.<sup>1</sup> The main cause being identified as the combustion of fossil fuels. Methods that involve reducing the amount of CO<sub>2</sub> released into the atmosphere from industrial processes are therefore of significant value.<sup>2</sup> Current commercial methods involve CO<sub>2</sub> capture *via* absorption using amine based materials post combustion.<sup>3</sup> Pre-combustion methods also exist in which fuel is firstly converted into H<sub>2</sub> and CO<sub>2</sub> followed by a capture process. Once captured storage of CO<sub>2</sub> is achieved by storing it in unused oil/gas wells or under the ocean. This is a highly energy intensive process and unlike other waste streams CO<sub>2</sub> has a variety of possible uses such as a C1 building block in organic synthesis.<sup>4,5</sup>

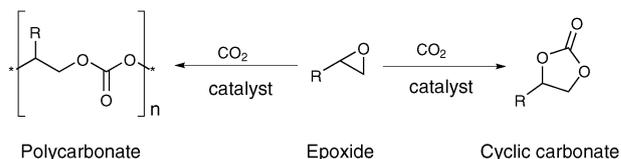
To chemists carbon dioxide presents itself as a cheap, non-toxic and highly abundant carbon source, and if effectively activated can allow for carboxylation of organic molecules. Therefore fixation of CO<sub>2</sub> into organic molecules is an area of increasing interest and offers a much more environmentally sound alternative to current storage solutions.<sup>6</sup> Currently, the greatest obstacle for establishing industrial processes based on CO<sub>2</sub> as a raw material is that in general a large energy input is required to transform CO<sub>2</sub>.

There are several useful products which can be prepared from CO<sub>2</sub>, for example polycarbonates, which are also synthesised from epoxides and CO<sub>2</sub> (Scheme 1), are commercially important as they have several applications, for example as eyewear lenses and exterior automotive components.<sup>7</sup> Perhaps

the two most effective solutions have been reported independently by Coates and Lee. Coates zinc based catalyst **1** has been employed in the copolymerisation of cyclohexene oxide and CO<sub>2</sub><sup>8</sup> and Lee's salen cobalt catalyst **2** has been used in the copolymerisation of propylene oxide and CO<sub>2</sub> (Fig. 1).<sup>9</sup> Cyclic carbonates, which are also produced from epoxides and CO<sub>2</sub>, are widely used in the manufacture of products including solvents, paint-strippers, biodegradable packaging, as well as having other applications in the chemical industry.<sup>10</sup> Again, however, these processes do require high energy input, including high temperatures, high pressures and the use of purified carbon dioxide.

There are a plethora of methods for the formation of cyclic carbonates from epoxides and CO<sub>2</sub><sup>11</sup> but recent efforts have been focused on the development of catalytic systems which are able to transform epoxides to cyclic carbonates at temperatures below 100 °C and at atmospheric pressure. Currently the only successful system is that reported by North and co-workers which employs a bimetallic salen complex such as **3** (Fig. 1) and tetrabutylammonium bromide as a co-catalyst,<sup>12</sup> although later developments have incorporated the co-catalyst into the salen substructure.<sup>12c</sup>

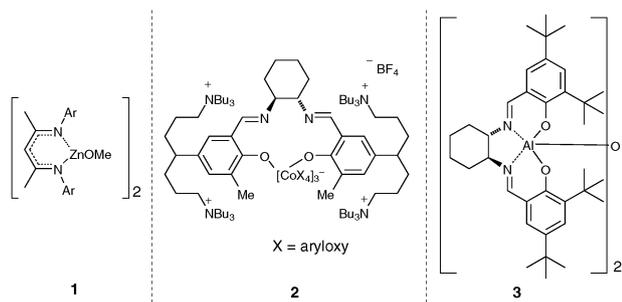
We were interested in developing a low energy alternative in line with our current research portfolio aimed at electrosynthesis<sup>13</sup> coupled with semiconductor photoelectrodes to drive light assisted electrosynthetic reactions.<sup>14</sup> We were therefore attracted to the possibility of employing an electrosynthetic system as this type of process could be designed to be cost neutral in terms of energy consumption if combined with a suitable solar powered energy source. Duñach has previously reported the electrochemical carboxylation of epoxides using a nickel(II) cyclam complex,<sup>15</sup> and in a related process Yuan and co-workers have reported an electrochemical system using high CO<sub>2</sub> pressures.<sup>16</sup> Both of these systems unfortunately have several drawbacks, including expensive potentially toxic catalysts, non-user friendly solvents and in the latter case high CO<sub>2</sub> pressures.



**Scheme 1** Current processes for CO<sub>2</sub> incorporation into epoxides.

Department of Chemistry, Loughborough University, Loughborough, Leicestershire, LE11 3TU, UK. E-mail: b.r.buckley@lboro.ac.uk, u.wijayantha@lboro.ac.uk; Fax: (+) +44 (0)1509 22 3925

† Electronic supplementary information (ESI) available: Experimental procedures and characterization of compounds **5a–k**. See DOI: 10.1039/c1cc15467b

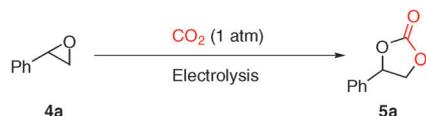


**Fig. 1** Current catalysts for CO<sub>2</sub> incorporation into epoxides.

We believed that it should be possible to deliver a step change in this technology by the development of an electrochemical system which is easy to set up, cheap, reliable, requires no expensive catalysts, runs under atmospheric CO<sub>2</sub> pressures and at ambient temperatures. In order to achieve this goal we set about screening a range of electrode materials for the electrosynthetic incorporation of CO<sub>2</sub> into our test substrate styrene oxide **4a** (Table 1). The reactions were run in a single compartment cell, with acetonitrile as solvent, tetrabutylammonium bromide as electrolyte and 60 mA current. We were delighted to find that good to excellent conversions to cyclic carbonate could be achieved under a variety of conditions (Table 1). Excellent conversion to cyclic carbonate **5a** was achieved using the copper cathode/magnesium anode combination (Table 1, entry 1). It is important to note that in the absence of applied current we observed little to no cyclic carbonate (3%) and only recovered unreacted epoxide.<sup>17</sup> We also did not observe the formation of any polymeric materials from the possible competing polycarbonate reaction or any other side products that have previously been observed for the corresponding reactions carried out at high temperature and/or pressure.<sup>18,19</sup>

We next turned our attention to optimizing this mild system (Table 2), we found that high conversion to cyclic carbonate could still be achieved if we reduced the amount of tetrabutylammonium bromide to 1.0 equivalent (it is important to note

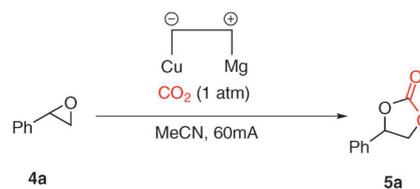
**Table 1** Electrode screening<sup>a</sup>



Entry	Cathode	Anode	Conv. (%) <sup>b,c</sup>
1	Cu	Mg	>99 (3)
2	Steel	Mg	75
3	Graphite	Mg	80
4	Cu	Al	75
5	Cu	Sn	10
6	Cu	Zn	5

<sup>a</sup> General conditions: CO<sub>2</sub> (1 atm, balloon), Bu<sub>4</sub>NBr (2.0 eq.), MeCN, single compartment cell, 60 mA, 7 h rt, 12 h 50 °C. <sup>b</sup> Conversion evaluated from the <sup>1</sup>H NMR spectrum by integration of epoxide vs. cyclic carbonate peaks. <sup>c</sup> The number in parenthesis refers to the conversion from the reaction carried out in the absence of electrolysis.

**Table 2** Optimization studies<sup>a</sup>



Entry	Supporting electrolyte (equiv.)	T/°C	t (h)	Conv. (%) <sup>b</sup>
1	Bu <sub>4</sub> NBr (2.0)	7 h rt, 12 h 50 °C	19	>99
2	Bu <sub>4</sub> NBr (1.0)	7 h rt, 12 h 50 °C	19	98
3	Bu <sub>4</sub> NBr (0.5)	7 h rt, 12 h 50 °C	19	80
4	Bu <sub>4</sub> NBr (1.0)	25 °C	6	77
5	Bu <sub>4</sub> NPF <sub>6</sub> (1.0)	50 °C	6	17
6	Bu <sub>4</sub> NBr (1.0) <sup>c</sup>	50 °C	6	99 (96)
7	Bu <sub>4</sub> NBr (1.0)	25 °C	6	77
8	Bu <sub>4</sub> NBr (1.0)	50 °C	3.5	76

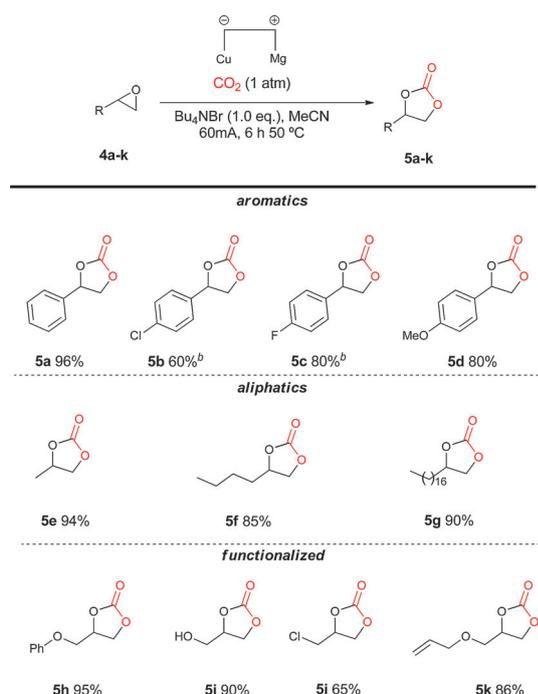
<sup>a</sup> General conditions: Cu cathode, Mg anode, CO<sub>2</sub> (1 atm, balloon), MeCN, single compartment cell, 60 mA. <sup>b</sup> Conversion evaluated from the <sup>1</sup>H NMR spectrum by integration of epoxide vs. cyclic carbonate peaks, isolated yield after column chromatography is shown in parenthesis. <sup>c</sup> On average 90–95% of the Bu<sub>4</sub>NBr is recovered after each reaction by precipitation with EtOAc.

here that we typically recover 90–95% of this material after the reaction by precipitation with EtOAc), however, below this level we observed only 80% conversion (Table 2, entry 3). We also found that the use of tetrabutylammonium bromide is essential for the reaction to proceed, if we replaced the bromide counter-ion with tetrafluoroborate then we observed only 17% conversion to cyclic carbonate (Table 2, entry 5). The reactions can be carried out at room temperature (77% conversion after 6 h, Table 2, entry 7), however, for convenience mild heating to 50 °C is employed (Table 2, entry 6); A combination of heating (50 °C) and electrolysis (60 mA) affords the cyclic carbonate **2a** in 99% conversion and 96% isolated yield. Reduced reaction times, for example, 3.5 h results in only 76% conversion (Table 2, entry 8).

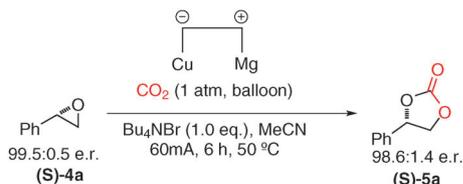
With our optimized conditions in hand we screened the applicability of this system over a range of substrate types (Table 3). We were delighted to find that excellent yields of cyclic carbonates were observed, including electron rich and poor aromatic systems, and a range of aliphatic epoxides were also effectively converted to the corresponding cyclic carbonate (these yields represent some of the highest reported to date). Sensitive functionalized substrates such as **4i–k**, are also tolerated under the reaction conditions affording excellent yields of the corresponding cyclic carbonates **5i–k**.

In order to explore the mild nature of these reaction conditions we were interested in the applicability of this system to enantiopure epoxides. Application of our optimized conditions to the CO<sub>2</sub> incorporation of (*S*)-styrene oxide afforded the cyclic carbonate in excellent yield (97%) with retention of configuration and only a slight loss of optical purity (99.5:0.5 e.r. to 98.6:1.4 e.r., (Scheme 2)).

In conclusion we have developed a powerful new tool in the combat against CO<sub>2</sub> emissions for the synthesis of value added compounds. This process is one of only a handful of

**Table 3** Application to a range of epoxides<sup>a</sup>

<sup>a</sup> General conditions: CO<sub>2</sub>, Cu cathode, Mg anode, Bu<sub>4</sub>NBr (2.0 equiv.), MeCN, single compartment cell, 60 mA, 6 h 50 °C, isolated yields shown are after column chromatography. <sup>b</sup> Reaction ran for 8 h.



**Scheme 2** Electrococarbonylation of (*S*)-styrene oxide to afford the enantiomerically pure cyclic carbonate with retention of configuration.

approaches that allow this reaction to proceed at atmospheric pressure and at ambient-mild temperatures.<sup>11,15</sup> The yields obtained are comparable or better than those already reported in the area and our approach benefits from not employing an additional catalyst into the reaction, which in some cases can be toxic or expensive. The equipment required to perform this CO<sub>2</sub> incorporation reaction is cheap and should be readily available in any undergraduate teaching facility *i.e.* copper wire, magnesium ribbon and a power supply. We are currently looking at the mechanism (early indications show that it does not involve MgBr<sub>2</sub><sup>20</sup> but may well be related to that postulated by North and co-workers)<sup>12e</sup> and scalability of this process<sup>21</sup> as well as applications of CO<sub>2</sub> incorporation towards other types of organic molecules and the development of a self-contained solar driven process.

B.R.B. and K.G.U.W. would like to thank Research Councils UK for RCUK fellowships and Loughborough University for funding a PhD studentship to A.P.P.

## Notes and references

- (a) H. Yang, Z. Xu, M. Fan, R. Gupta, R. B. Slimane, A. E. Bland and I. Wright, *J. Environ. Sci.*, 2008, **20**, 14–27; (b) The 2010 BP statistical review of world energy (<http://www.bp.com/statisticalreview>).
- D. P. Schrag, *Science*, 2007, **315**, 812–813.
- P. H. M. Feron and C. A. Hendriks, *Oil Gas Sci. Technol.*, 2005, **60**, 451–459.
- T. Sakakura, J.-C. Choi and H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365–2387.
- M. Aresta and A. Dibenedetto, *Dalton Trans.*, 2007, 2975–2992.
- R. Angamuthu, P. Byers, M. Lutz, A. L. Spek and E. Bouwman, *Science*, 2010, **327**, 313–315.
- V. Serini, “Polycarbonates”, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, 2000.
- D. R. Moore, M. Cheng, E. B. Lobkovsky and G. W. Coates, *Angew. Chem., Int. Ed.*, 2002, **41**, 2599.
- J. Yoo, S. J. Na, H. C. Park, A. Cyriac and B. Y. Lee, *Dalton Trans.*, 2010, **39**, 2622–2630.
- M. North, R. Pasquale and C. Young, *Green Chem.*, 2010, **12**, 1514–1539.
- For some recent reviews and articles on high pressure and/or temperature approaches to cyclic carbonates see: (a) I. Omae, *Catal. Today*, 2006, **115**, 33–52; (b) J. H. Clements, *Ind. Eng. Chem. Res.*, 2003, **42**, 663–674; (c) M. Yoshida and M. Ihara, *Chem.–Eur. J.*, 2004, **10**, 2886–2893; (d) R. Srivastava, T. H. Bennur and D. Srinivas, *J. Mol. Catal. A: Chem.*, 2005, **226**, 199–205; (e) R. Zevenhoven, S. Eloneva and S. Teir, *Catal. Today*, 2006, **115**, 73–79; (f) T. Sakakura and K. Kohno, *Chem. Commun.*, 2009, 1312–1330; (g) J. Sun, S.-i. Fujita and M. Arai, *J. Organomet. Chem.*, 2005, **690**, 3490–3497; (h) W.-L. Dai, S.-L. Luo, S.-F. Yin and C.-T. Au, *Appl. Catal., A*, 2009, **366**, 2–12; (i) R. L. Paddock and S. T. Nguyen, *J. Am. Chem. Soc.*, 2001, **123**, 11498–11499.
- (a) J. Meléndez, M. North and R. Pasquale, *Eur. J. Inorg. Chem.*, 2007, 3323–3326; (b) M. North and R. Pasquale, *Angew. Chem.*, 2009, **121**, 2990–2992 (*Angew. Chem., Int. Ed.*, 2009, **48**, 2946–2948); (c) J. Meléndez, M. North and P. Villuendas, *Chem. Commun.*, 2009, 2577–2579; (d) M. North, P. Villuendas and C. Young, *Chem.–Eur. J.*, 2009, 11454–11457; (e) W. Clegg, R. W. Harrington, M. North and R. Pasquale, *Chem.–Eur. J.*, 2010, **16**, 6828–6843; (f) I. S. Metcalfe, M. North, R. Pasquale and A. Thursfield, *Energy Environ. Sci.*, 2010, **3**, 212–215.
- P. C. B. Page, F. Marken, C. Williamson, Y. Chan, B. R. Buckley and D. Bethell, *Adv. Synth. Catal.*, 2008, **350**, 1149–1154.
- (a) A. A. Tahir and K. G. U. Wijayantha, *J. Photochem. Photobiol., A*, 2010, **216**, 119–125; (b) A. A. Tahir, K. G. U. Wijayantha, S. Saremi-Yarahmadi, M. Mazhar and V. McKee, *Chem. Mater.*, 2009, **21**, 3763–3772; (c) K. Tennakone, G. R. R. A. Kumara, K. G. U. Wijayantha, I. R. M. Kottegoda, V. P. S. Perera and M. L. P. Aponso, *J. Photochem. Photobiol., A*, 1997, **108**, 175–177.
- (a) P. Tascadda and E. Duñach, *J. Chem. Soc., Chem. Commun.*, 1995, 43–44; (b) E. Duñach, P. Tascadda, M. Weidmann and E. Dinjus, *Appl. Organomet. Chem.*, 2001, **15**, 141–144.
- Y. Wang, G.-Q. Yuan, Y.-C. Zeng and H.-F. Jiang, *Chin. J. Org. Chem.*, 2007, **27**, 1397–1400.
- Epoxides dissolved in molten TBAB/TBAI have been converted into cyclic carbonates under atmospheric pressure carbon dioxide, but at elevated temperatures (120 °C): see V. Calo, A. Nacci, A. Monopoli and A. Fanizzi, *Org. Lett.*, 2002, **4**, 2561–2563.
- For example, isomerisation of the epoxide to ketone and aldehydes or addition of H<sub>2</sub>O to afford the ring opened diol: see J.-Q. Wang, X.-D. Yue, F. Cai and L.-N. He, *Catal. Commun.*, 2007, **8**, 167–172.
- GC-MS and <sup>1</sup>H, <sup>13</sup>C NMR data revealed only the reaction products and Bu<sub>4</sub>NBr.
- In an independent reaction addition of MgBr<sub>2</sub> to the reaction without electrolysis resulted in complete recovery of starting materials.
- The electrode materials required for large scale applications are currently commercially available. Mg anodes are used in the protection of ship hulls. See for example: <http://www.corrpro.co.uk/pdf/Anodes/Magnesium/Magnesium-Anodes.pdf>.