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Direct Electrosynthesis of Organic Carbonates from CO_2 with Alcohols Under Mild Condition

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Electrosynthesis of organic carbonates from CO_2 with alcohols has been carried out directly under galvanostatic condition at room temperature and normal pressure in DMF/MeCN without any additional catalyst. For the model compound methanol, the influence of solvents, electrode materials, current densities, charge amount, temperature and MeOH concentration have been investigated. Primary and second alcohols are converted into corresponding linear organic carbonates with moderate and low yields, whereas tertiary alcohol and phenol are unreactive. Moreover, cyclic carbonates could be synthesized from CO_2 and diols.

Keywords: Alcohols, Carbon dioxide, Electrosynthesis, Organic carbonates

1. INTRODUCTION

Organic carbonates are a very important class of compounds whose versatility allows their applications in several fields of the chemical and pharmaceutical industry, such as the production of engineering plastics, electrolyte solvents for lithium ion batteries, organic solvents, fuel additives and green reagents, etc.[1] For the widespread applications of organic carbonates, the synthesis methodologies, both for linear and cyclic carbonates, have been extensively discussed and reviewed in the past decades.[2-4] The most important way is phosgenation technique, by which high yields of carbonates could be synthesized. However, toxic and corrosive reagent, phosgene, has to be used. And oxidative carbonylation of alcohols/phenols is also a useful method besides the use of CO.

Compared with other methods, the synthesis of organic carbonates from CO_2 and alcohols is one of the promising projects in the development of an environmentally benign process based on the utilization of a naturally abundant carbon resource. Meanwhile, CO_2 is the largest contributor to the greenhouse effect, while it is also recognized to be an easily available, cheap, recyclable and non-toxic carbon source, which makes it more and more important from the ecological and economic points of view to chemical fixation and utilization of CO_2. Recently, the synthetic technologies leading to organic carbonates using CO_2 as a raw material have been reported.[5,6] Although kinds of organic carbonates could be synthesized, drastic conditions and/or metal catalysts have to be used to activate CO_2, which is the thermodynamically stable carbon source.[7-12] Electrochemistry as an effective and green method to reduce, activate and utilize CO_2 at room temperature and normal pressure, some relative study have been widely reported.[13,14] In previous researches, organic carbonates and carbamates could be synthesized by one-electron reduction of dioxygen performed in aprotic dipolar solvents in the presence of carbon dioxide. [15-18] Organic carbonates could also be obtained from CO_2 and alcohols by electrogenerated bases (EGBs) electroreduced suitable porbases.[19] However, with the growing demand for environmental friendly processes, efforts need to be devoted to utilize the greenhouse gas and reduce multiple steps in the synthesis process. During our studies on CO_2 fixation to produce valuable chemicals, [20-28] we reported synthesis of dimethyl carbonate (DMC) by direct electrochemical activation of CO_2 in ionic liquid[26] and [Bmim]BF_4-MeCN solvent,[27] as well as synthesis of cyclic carbonates via direct electrochemical reduction of CO_2 in ionic liquid.[28] Here, as one of our continuing work, we succeeded in direct electrosynthesis of DMC from CO_2 and methanol in DMF/MeCN under galvanostatic electrolysis. Furthermore, the electrochemical reaction was extended to other alcohols and 1, 2-diols to synthesis linear and cyclic organic carbonates.

2. EXPERIMENTAL

2.1.Reagents

MeCN and DMF were kept over 4 Å molecular sieves. MeOH, benzyl alcohol, 2-phenylethanol, 3-phenyl-1-propanol, 1-phenylethanol, 1-phenyl-2-propanol, cyclohexanol, 2-phenyl-2-propanol, phenol, ethylene glycol, 1,2-propanediol, 1,2-butanediol, 1,2-pentanediol, 1,2-heptanediol, 2,3-butanediol, 1-phenyl-1,2-ethanediol, diethyl ether, potassium carbonate, magnesium sulphate androus, methyl iodide and distilled water were used as received.

2.2. Cyclic voltammetry and general electrosynthesis

Cyclic voltammetric studies were undertaken wih CHI 600c electrochemical workstation (Chenhua, shanghai, China). A conventional three-electrode cell was employed with Cu disk working electrode (d = 2 mm), a Pt wire counter electrode and a Ag/AgI/0.1 mol L^{-1} TBAI reference electrode.

Galvanostatic electrolysis was carried out in a mixture of MeOH (0.15 mol L^{-1}) and TBAI (0.1 mol L^{-1}) in 15 mL dry DMF/MeCN under a slow stream of CO_2 in a one-compartment electrochemical cell equipped with a graphite (C) anode and a copper (Cu) cathode until 1.0 F mol^{-1} of charge was passed. The electrolyte was esterified by adding anhydrous K_2CO_3 (0.1 mol L^{-1}) and MeI (0.5 mol L^{-1}) and the mixture was stirred at 50 ^{o}C for 5 h. Then the solution was distilled to obtain DMC (when the substrate was not methanol, the solution was hydrolyzed and extracted with Et_2O, and the organic layers was washed with H_2O, dried over $MgSO_4$, and then evaporated. The pure products were isolated by column chromatography using petroleum ether/ethyl acetate mixture as an eluent). The main features of the aimed products identified by HP 6890/5973N GC/MS (Agilent, USA), and AVANCE 500 NMR (Bruker, Germany) and the yields were determined by GC-2014 (Shimadazu, Japan).

Benzyl methyl carbonate 2b GC-MS (m/z, %) 166 (M$^+$, 55), 135 (1), 121 (18), 107 (43), 91 (100), 77 (27), 65 (18), 51(12), 39 (9); ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.82 (s, 3H), 5.19 (s, 2H), 7.36-7.42 (m, 5H).

Methyl phenethyl carbonate 2c GC-MS (m/z, %) 122 (1), 104 (100), 91 (18), 77 (8), 65 (7), 59 (5), 45 (3); ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.00 (t, J=7Hz, 2H), 3.78 (s, 3H), 4.37 (t, J=7Hz, 2H), 7.24-7.35 (m , 5H).

Methyl 3-phenylpropyl carbonate 2d GC-MS (m/z, %) 164 (1), 136 (1), 117 (100), 103 (9), 91 (66), 77 (11), 65 (13), 51 (7), 39 (6); ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.03 (q, J=7Hz, 2H), 2.74 (t, J=8Hz, 2H), 3.81 (s, 3H), 4.18 (t, J=7Hz, 2H), 7.20-7.32 (m, 5H).

Methyl 1-phenylethyl carbonate 2e GC-MS (m/z, %) 180 (M$^+$, 21), 121 (21), 104 (100), 91 (14), 77 (57), 51 (29); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.62 (d, J=7Hz, 3H), 3.77 (s, 3H), 5.76 (q, J=7Hz, 1H), 7.31-7.41 (m, 5H).

Methyl (1-phenylpropan-2-yl) carbonate 2f GC-MS (m/z, %) 179 (1), 149 (1), 135 (1), 118 (100), 103 (5), 91 (76), 77 (6), 65 (13), 51 (6), 39 (7); ^{1}H-NMR (500 MHz, $CDCl_3$, 500Hz): δ 1.28 (d, J=6Hz, 3H), 2.78(q, J=7Hz,1H), 3.00(q, J=7Hz, 1H), 3.74(s, 3H), 4.94-5.00(m, 1H), 7.20-7.31(m, 5H).

Cyclohexyl methyl carbonate 2g GC-MS (m/z, %) 115 (1), 99 (24), 82 (94), 67(100),55 (53), 41 (50); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.24-1.28 (m, 1H), 1.31-1.40 (m, 2H), 1.43-1.55 (m, 3H), 1.73-1.76 (m, 2H), 1.89-1.93 (m, 2H), 3.76 (s, 3H)，4.58-4.63 (m, 1H).

4-Ethyl-[1,3] dioxolan-2-one 4c GC-MS (m/z, %) 116 (M$^+$, 4), 87 (64), 71 (4), 57 (15), 43 (100); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.04 (t, J=8Hz, 3H), 1.73-1.86 (m, 2H), 4.10 (t, J=8Hz, 1H), 4.54 (t, J=8Hz, 1H), 4.67 (q, J=7Hz, 1H).

4-popyl-[1,3] dioxolan-2-one 4d GC-MS (m/z, %) 129 (1), 102 (1), 87 (67), 71 (20), 57 (40), 43 (100); ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.99 (t, J=7Hz, 3H), 1.42-1.44 (m, 1H), 1.50-1.53 (m, 1H), 1.66-1.69 (m, 1H), 1.80-1.82 (m, 1H), 4.08 (t, J=8Hz, 1H), 4.54 (t, J=8Hz, 1H), 4.70-4.76 (m, 1H).

4-Pentyl-[1,3] dioxolan-2-one 4e GC-MS (m/z, %) GC-MS (m/z, %) 130 (1), 116 (1), 103 (3), 87 (24), 71 (33), 58 (57), 43 (100); ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.90 (t, J=7Hz, 3H), 1.33-1.38 (m, 5H), 1.47-1.49 (m, 1H), 1.66-1.70 (m, 1H),1.80 (q, J=5Hz, 1H), 4.07 (t, J=8Hz, 1H), 4.53 (t, J=8Hz, 1H), 4.68-4.74 (m, 1H).

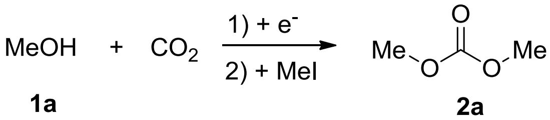
4-Phenyl-[1,3] dioxolan-2-one 4f GC-MS (m/z, %) 164 (M$^+$, 66), 131 (1), 119 (15), 105 (32), 90 (100), 78 (71), 65 (19), 51 (25), 39 (13); ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.36 (t, J=9Hz, 1H), 4.83 (t, J=9Hz, 1H), 5.69 (t, J=8Hz, 1H), 7.27-7.48 (m, 5H).

4,5-Dimethyl-[1,3] dioxolan-2-one 4g GC-MS (m/z, %) 116 (M^+, 3), 101 (4), 86 (1), 73 (3), 57 (7), 51 (2), 43 (100), 38 (6), 28 (78); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.46 (q, J=6Hz, 6H), 4.32-4.35 (m, 2H).

3. RESULTS AND DISSCUSION

3.1. Electrosynthesis of dimethyl carbonate from CO_2 with methanol

Methanol (1a) was first chosen as the model compound to be investigated in this study. The electrolysis was carried out in CO_2-saturated DMF/MeCN solution containing 0.15 mol L^{-1} 1a in an undivided cell with C anode and Cu cathode under constant current until 1.0 F mol^{-1} of the charge of 1a passed. After esterification, dimethyl carbonate (DMC, 2a) was obtained as the main product (Scheme 1). To optimize the yield, the effects of various synthetic parameters on the process such as solvents, electrode materials, current densities, charge amount, temperature and methanol concentration were investigated. The results of the electrolysis are summarized in Table 1.



Scheme 1. Electrosynthesis of dimethyl carbonate from CO_2 and methanol.

To investigate the effect of solvent, the electrolysis was conducted in both DMF and MeCN (Table 1, entries 1-2). The results show that higher DMC yield was obtained in MeCN which may attribute to the larger solubility of CO_2 in MeCN compared with DMF.[29]

The nature of the electrode material may strongly influence the reduction of CO_2.[30] Accordingly a set of electrolysis was carried out with different cathodes and the results were listed in Table 1 (Entries 2-6). The DMC yield decreased depending on the employed cathode materials in the following order: Cu > Ag> Ni> Ti> Stainless steel. Thus, Cu is recognized as the best material for this reaction system.

The electroreduced species $CO_2^{\cdot-}$ is not very stable in the solution. Some species, such as aldehyde, acid, could still be produced during the electrolysis, which could reduce the faraday efficiency. Therefore, the effect of charge amount should be investigated to find the suitable electrolysis condition. A set of electrolysis was carried out from 0.5 to 2.0 F mol^{-1} (Table 1, entries 2 and 7-10). Before 1.0 F mol^{-1}, the DMC yield was increased linearly with charge amount. After then, the yield was decreased to 22 % for 2.0 F mol^{-1}, which may attribute to the further reduce of the produced carbonate.[31].

The yields are also affected by the current density (Table 1, entries 2, 11-14). When the current density was increased from 2.86 to 4.14 mA cm^{-2}, the DMC yield was increased from 23 to 31 %.

While the current density was increased continuously to 5.38mA cm^{-2}, the DMC yield was decreased to 20 %. The results indicate that the optimized current density is 4.14 mA cm^{-2}.

Table 1. Electrosynthesis of dimethyl carbonate (2a) from CO_2 and MeOH (1a) under various synthetic conditions [a]

Entry	Solvent	Electrode	Q (F mol^{-1})	j (mA cm^{-2})	Temperature (°C)	C_{MeOH} (mol L^{-1})	Yield[b] (%)
1	DMF	Cu-C	1.0	4.14	25	0.15	21
2	MeCN	Cu-C	1.0	4.14	25	0.15	31
3	MeCN	Ag-C	1.0	4.14	25	0.15	25
4	MeCN	Ti-C	1.0	4.14	25	0.15	16
5	MeCN	Ni-C	1.0	4.14	25	0.15	23
6	MeCN	Ss-C	1.0	4.14	25	0.15	9
7	MeCN	Cu-C	0.5	4.14	25	0.15	12
8	MeCN	Cu-C	0.8	4.14	25	0.15	20
9	MeCN	Cu-C	1.5	4.14	25	0.15	28
10	MeCN	Cu-C	2.0	4.14	25	0.15	22
11	MeCN	Cu-C	1.0	2.86	25	0.15	23
12	MeCN	Cu-C	1.0	3.50	25	0.15	26
13	MeCN	Cu-C	1.0	4.75	25	0.15	24
14	MeCN	Cu-C	1.0	5.38	25	0.15	20
15	MeCN	Cu-C	1.0	4.14	0	0.15	21
16	MeCN	Cu-C	1.0	4.14	15	0.15	28
17	MeCN	Cu-C	1.0	4.14	40	0.15	23
18	MeCN	Cu-C	1.0	4.14	25	0.05	16
19	MeCN	Cu-C	1.0	4.14	25	0.10	25
20	MeCN	Cu-C	1.0	4.14	25	0.20	30
21	MeCN	Cu-C	1.0	4.14	25	0.30	17

[a] General conditions: supporting electrolyte TBAI = 0.1 mol L^{-1}, MeOH concentration = 0.15 mol L^{-1}, CO_2 pressure = 1 atm. [b] GC yields.

According to the literature,[29] the saturated concentration of CO_2 in MeCN was depended on the temperature. Normally, the lower the temperature is, the more CO_2 could be dissolved in MeCN. As CO_2 is a key reagent in this reaction, the concentration of CO_2, which in fact is depended on the temperature, may affect the DMC yield. On the other hand, the temperature will affect the over potential and reaction rate of the electrochemical reaction, which may affect the DMC yield too. In order to investigate the effect of temperature on this reaction, a set of electrolyses was performed in the range of 0 °C to 40 °C (Table 1**,** entries 2, 15-17). The best yield of 31 % was obtained at 25 °C.

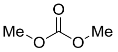
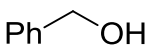
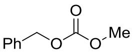
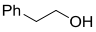
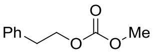
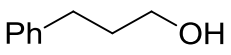
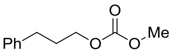
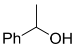
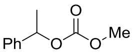
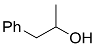
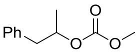
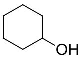
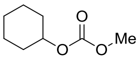
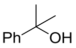
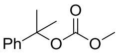
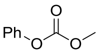
As MeOH is another key reagent, its concentration will affect the extent of reaction. Five different of MeOH concentration have been tried here to optimize the reaction condition (Table 1, entries 2, 18-21). When the concentration of MeOH was increased from 0.05 mol L^{-1} to 0.15 mol L^{-1}, the DMC yield was increased from 16 % to 31 %. While the concentration is continuously increased to

0.3 mol L^{-1}, the DMC yield was decreased to 17 %. At lower MeOH concentration the contact opportunity of 1a and CO_2 decreased resulted in lower yield. Too much 1a may favor the polymerization of MeOH to produce dimethyl ether,[32] which resulted in a decrease of the yield. So the optimized MeOH concentration is 0.15 mol L^{-1}.

3.2. Electrosynthesis of other linear carbonates from CO_2 with alcohols (R_1OH)

To test the effectiveness and generality of this methodology, we extended the investigation to other alcohols 1b–i, carrying out the reactions under the previous optimized conditions. The results of analyses are reported in Table 2 and some conclusions can be drawn. The primary alcohols 1a-d are converted into the corresponding linear organic carbonates 2a-d with moderate yields (Table 2, entries 1-4). Under the same condition, the secondary alcohols 1e-g give lower yields of linear carbonates 2e-g (Table 3, entries 5-7). In the case of tertiary alcohol 1h and phenol 1i, no supposed carbonates could be detected. That's mainly because of the steric hindrance and/or the unfavourable reaction between carbon dioxide radical anion and 1h-i to form carbonate.

Table 2. Electrosynthyesis of linear carbonates 2a-i from carbon dioxide and alcohols 1a-i. [a]

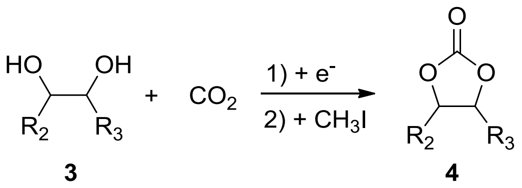
Entry	Alcohols		Linear carbonates		Yield [b] (%)
1	MeOH	1a		2a	31
2		1b		2b	30
3		1c		2c	32
4		1d		2d	31
5		1e		2e	18
6		1f		2f	16
7		1g		2g	19
8		1h		2h	----
9	Ph–OH	1i		2i	----

[a] General conditions: MeCN = 15 mL, TBAI = 0.1 mol L^{-1}, C_{ROH} = 0.15 mol L^{-1}, j = 4.14 mA cm^{-2}, Q = 1 F mol^{-1}, T = 25 °C, cathode = Cu, anode = graphite, CO_2 pressure= 1 atm. [b] GC yield.

3.3. Electrosynthesis of cyclic carbonates from diols

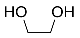
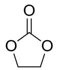
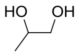
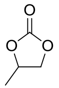
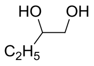
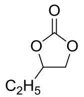
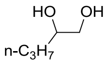
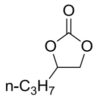
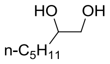
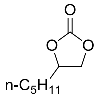
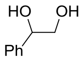
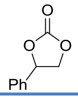
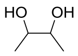
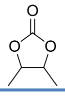
Then, the investigation was extended from alcohols to diols 3. In all cases, cyclic organic carbonates 4 have been detected as the main products (Scheme 2). The obtained results are listed in

Table 3. In the case of glycol 3a, 22 % of ethylene carbonate 4a was obtained (Table 3, entry 1). By changing one substituent group from H to one or more carbon atoms (3b-e), the carbonates yields were about 22 % (Table 3, entries 2-5). When one carbon atom was substituted by phenyl, 23 % of corresponding cyclic carbonate could be synthesized (Table 3, entry 6). Once both carbon atoms of 1,2-diol were substituted, such as 3g, a lower carbonate yield was obtained (Table 3, entry 7).



Scheme 2. Electrosynthesis of cyclic carbonates from CO_2 and diols.

Table 3. Electrosynthyesis of cyclic carbonates 4a-g from carbon dioxide and diols 3a-g. [a]

Entry	Diols		Cyclic carbonates		Yield [b] (%)
1		3a		4a	22
2		3b		4b	21
3		3c		4c	23
4		3d		4d	22
5		3e		4e	23
6		3f		4f	23
7		3g		4g	17

[a] General conditions: MeCN = 15 mL, TBAI = 0.1 mol L^{-1}, C_{diol} = 0.15 mol L^{-1}, j = 4.14 mA cm^{-2}, Q = 1 F mol^{-1}, T = 25 °C, cathode = Cu, anode = graphite, CO_2 pressure= 1 atm. [b] GC yield.

3.4. Electrochemical reaction pathway

Cyclic voltammetry has been used to investigate the electrochemical behaviour of the reactants. As shown in Fig. 2, no peak could be detected after addition of 0.01 mol L^{-1} MeOH (curve b), compare to the background (curve a). When the DMF solution was saturated with CO_2, an irreversible reduction peak is found at -2.4 V (curve c), which is ascribed to the electrochemical reduction of CO_2 to $CO_2^{\cdot -}$.[33]

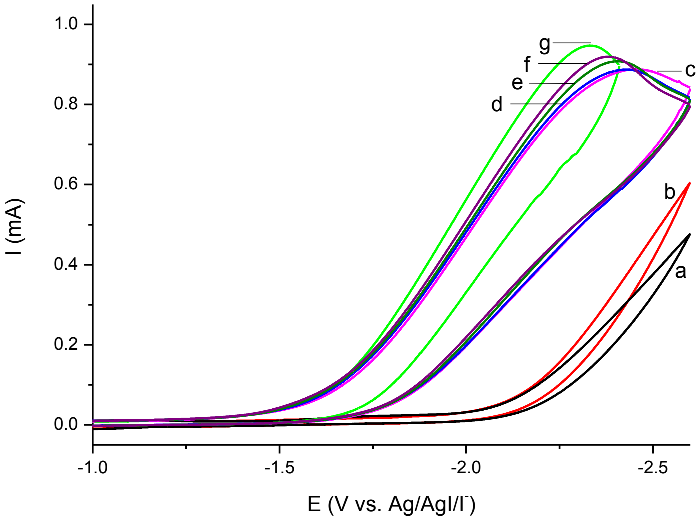


Figure 1. Cyclic voltammograms on Cu electrode at 0.1 V s^{-1} in DMF-0.1 mol L^{-1} TEABF$_4$ solution: (a) DMF solution; (b) DMF containing 0.01 mol L^{-1} MeOH; (c) DMF saturated with CO$_2$ (0.2 mol L^{-1}); (d) DMF containing 0.01 mol L^{-1} MeOH saturated with CO$_2$; (e) DMF containing 0.05 mol L^{-1} MeOH saturated with CO$_2$; (f) DMF containing 0.1mol L^{-1} MeOH saturated with CO$_2$; (g) DMF containing 0.2 mol L^{-1} MeOH saturated with CO$_2$

After addition of 0.01 M MeOH into the CO$_2$ saturated DMF solution, the reduction peak moved positively with increased peak current (curve d). Moreover, by increasing the MeOH concentration, the reduction peak further shifts to positive with the peak current more increased (curve e-g). It indicates that alcohol could react with $CO_2^{\cdot -}$ radical anion which was generated firstly during the electrolysis process to form carbonate anion.

Comparative electrolysis was also carried out to further understand the electrosynthesis pathway. The obtained results are listed in Table 4. As described before, when the electrolysis was carried out in a solution containing both MeOH and CO$_2$, 31 % of DMC could be formed after the esterification (Table 4, entry 1).

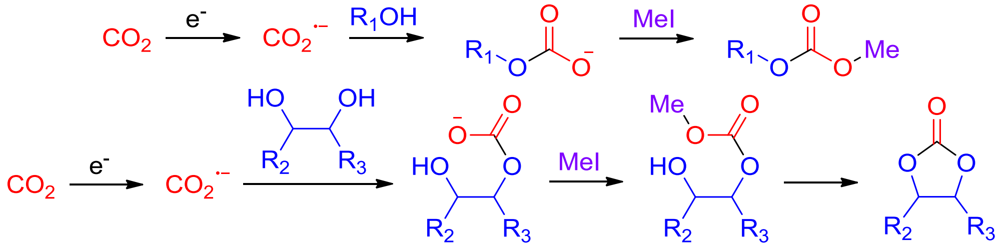
Table 4. Influence of other parameters on the electrosynthesis of DMC from CO$_2$ and MeOH [a]

Entry	Synthesis route	DMC Yield [b] (%)
1	$\mathrm{MeOH + CO_2} \xrightarrow[\text{MeCN-TBAI}]{\text{1) } e^-} \xrightarrow{\text{2) MeI}}$	37
2	$\mathrm{MeOH} \xrightarrow[\text{MeCN-TBAI}]{\text{1) } e^-} \xrightarrow{\text{2) } CO_2} \xrightarrow{\text{3) MeI}}$	----
3	$\mathrm{CO_2} \xrightarrow[\text{MeCN-TBAI}]{\text{1) } e^-} \xrightarrow{\text{2) MeI}}$	----
4	$\mathrm{CO_2} \xrightarrow[\text{MeCN-TBAI}]{\text{1) } e^-} \xrightarrow{\text{2) MeOH}}$	----

[a] General conditions: MeCN = 15 mL, TBAI = 0.1 mol L^{-1}, C_{MeOH} = 0.15 mol L^{-1}, j = 4.14 mA cm^{-2}, Q = 1 F mol^{-1}, T = 25 ^{o}C, cathode = Cu, anode = graphite, CO$_2$ pressure= 1 atm. [b] GC yield.

However, no DMC could be detected, when CO_2 was bubbled into solution (MeCN - 0.1 mol L^{-1} TBAI -0.15 mol L^{-1} MeOH) after electrolysis (Table 4, entry 2). The reason is that MeOH is hard to be electroreduced, which could also be confirmed by previous CVs. We also tried the reaction without MeOH or MeI, no DMC could be synthesized in both cases (Table 4, entries 3-4), which indicates that both methyl group in MeOH and MeI were transferred into dimethyl carbonate. The other corresponding linear carbonates 2b-2g synthesized from alcohols 1b-1g shows that alcohols provide one alkyl group for linear carbonate, while another is from MeI.

Based on the above-discussed CVs and electrolysis as well as literature, a possible synthesis pathway was proposed (Scheme 3). In the case of alcohols, CO_2 was electroreduced firstly to corresponding radical anion, which was reacted with R_1OH to form a carbonate anion. At last, esterification by MeI completes the reaction to afford corresponding linear carbonate. Similar reactions could be achieved for diols. The only difference is the linear carbonates obtained from diols are unstable, which prefer converted to cyclic carbonate under the reaction condition.[16]



Scheme 3. Electrosynthesis pathway.

4. CONCLUSIONS

In conclusion, we have demonstrated a simple directly electrochemical route to synthesis of organic carbonates from CO_2 and alcohols/diols under mild condition. Various conditions, such as solvents, electrode materials, current densities, charge amount, temperature and alcohol concentration could affect the yield of organic carbonate. Under the optimized condition, 31 % of DMC could be synthesized. Under the same condition, linear carbonates could be obtained from primary and secondary alcohols, while diols were converted into cyclic carbonates. The electrosynthesis pathway was also proposed.

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References

1. P. Tundo, M. Selva, *Acc. Chem. Res.*, 35 (2002) 706-716
2. A.-A. G. Shaikh, S. Sivaram, *Chem. Rev.*,96 (1996) 951-976
3. M. North, R. Pasquale, *Angew. Chem. Int. Ed.*, 48 (2009) 2946-2948
4. D. Aymes, D. Ballivet-Tkatchenko, K. Jeyalakshmi, L. Saviot, S. Vasireddy, *Catal. Today*, 147 (2009) 62-67
5. T. Sakakura, K. Kohno, *Chem. Commun.*, (2009) 1312-1330
6. W. L. Dai, S. L. Luo, S. F. Yin, C. T. Au, *Appl. Catal. a-Gen.*, 366 (2009) 2-12
7. S. Wang, D. S. Mao, X. M. Guo, G. S. Wu, G. Z. Lu, *Catal. Commun.*, 10 (2009) 1367-1370
8. J. Bian, M. Xiao, S. J. Wang, Y. X. Lu, Y. Z. Meng, *Catal. Commun.*, 10 (2009) 1142-1145
9. Q. H. Cai, B. Lu, L. J. Guo, Y. K. Shan, *Catal. Commun.*, 10 (2009) 605-609
10. D. S. Bai, H. W. Jing, Q. Liu, Q. Q. Zhu, X. F. Zhao, *Catal. Commun.*, 11 (2009) 155-157
11. K. Almusaiteer, *Catal. Commun.*, 10 (2009)1127-1131
12. A. Kilic, M. Ulusoy, M. Durgun, Z. Tasci, I. Yilmaz, B. Cetinkaya, *Appl. Organomet. Chem.*, 24 (2010) 446-453
13. D. M. Rakowski, D. L. Dubois, *Acc. Chem. Res.*, 42 (2009) 1974-1982
14. E. B. Cole, P. S. Lakkaraju, D. M. Rampulla, A. J. Morris, E. Abelev, A. B. Bocarsly, *J. Am. Chem. Soc.*, 132 (2010) 11539-11551
15. M. A. Casadei, S. Cesa, M. Feroci, A. Inesi, L. Rossi, F. M. Moracci, *Tetrahedron*, 53 (1997) 167-176
16. M. A. Casadei, S. Cesa, M. Feroci, A. Inesi, *New J. Chem.*, 23 (1999) 433-436
17. M. A. Casadei, F. M. Moracci, G. Zappia, A. Inesi, L. Rossi, *J. Org. Chem.*, 62(1997) 6754-6759
18. M. A. Casadei, *Eur. J. Org. Chem.*, (2001) 1689-1693
19. M. A. Casadei, S. Cesa, L. Rossi, *Eur. J. Org. Chem.*, (2000) 2445-2448
20. H. Wang, G. R. Zhang, Y. Z. Liu, Y. W. Luo, J. X. Lu, *Electrochem. Commun.*, 9 (2007) 2235-2239
21. H. Wang, K. Zhang, Y. Z. Liu, M. Y. Lin, J. X. Lu, *Tetrahedron*, 64 (2008) 314-318
22. D. F. Niu, L. P. Xiao, A. J. Zhang, G. R. Zhang, Q. Y. Tan, J. X. Lu, *Tetrahedron*, 64 (2008) 10517-10520
23. K. Zhang, H. Wang, S. F. Zhao, D. F. Niu, J. X. Lu, *J. Electroanal. Chem.*, 630 (2009) 35-41.
24. K. Zhang, Y. J. Xiao, Y. C. Lan, M. X. Zhu, H. Wang, J. X. Lu, *Electrochem. Commun.*, 12 (2010) 1698-1702
25. H. Wang, K. Zhang, B. L. Chen, R. N. Li, J. Q. Zhao, J. X. Lu, *Int. J. Electrochem. Sci.*, 6 (2011) 1720-1729
26. L. Zhang, D. F. Niu, K. Zhang, G. R. Zhang, Y. W. Luo, J. X. Lu, *Green Chem.*, 10 (2008) 202-206
27. L. P. Xiao, G. R. Zhang, L. Zhang, D. F. Niu, J. X. Lu, *Chin. J. Catal.*, 30 (2009) 43-47
28. H. Wang, L. X. Wu, Y. C. Lan, J. Q. Zhao, J.X. Lu, *Int. J. Electrochem. Sci.*, 6 (2011) 4218-4227
29. A. Gennaro, A. A. Isse, E. Vianello, *J. Electroanal. Chem.*, 289 (1990) 203-215
30. M. Jitaru, D. A. Lowy, M. Toma, B. B. Toma, L. Oniciu, *J. Appl. Electrochem.*, 27 (1997) 875-889
31. D. D. Yuan, C. H. Yan, B. Lu, H. X. Wang, C. M. Zhong, Q. H. Cai, *Electrochim. Acta*, 54 (2009) 2912–2915
32. S. Fang, K. Fujimoto, *Applied Catalysis A: General*, 142 (1996) L1-L3.
33. M. Hammouche, D. Lexa, M. Momenteau, J. M. Saveant, *J. Am. Chem. Soc.*, 113 (1991) 8455-8466