Int. J. Electrochem. Sci., 6 **(2011)** 4218 - 4227

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Electrosynthesis of Cyclic Carbonates From CO_2 and Diols in Ionic Liquids Under Mild Conditions

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Received: 22 July 2011 / *Accepted:* 16 August 2011 / *Published:* 1 September 2011

A new electrochemical process for synthesis of cyclic carbonates from CO_2 and diols has been tested in CO_2-saturated room temperature ionic liquids (RTILs) for the first time. The synthesis has been carried out under mild and safe condition in undivided cell without any additional catalysts. The influence of reaction conditions, such as electrode materials, electrolysis potential, temperature, diol concentration and composition of RTILs, have been investigated. The recyclability of RTILs also has been confirmed. Moreover, the electrochemical reduction behavior has been studied by cyclic voltammetry.

Keywords: Carbon dioxide, cyclic carbonates, diols, electrosynthesis, ionic liquids

1. INTRODUCTION

The global warming due to the increased atmospheric CO_2 concentration resulting from increasing consumption of fossil fuel is becoming an important environmental issue today. After separation of CO_2 from its emission source, it is crucial adjective to fix and use this greenhouse gas [1]. Synthesis of organic carbonates from CO_2 is a very attractive method [2-4], which is not only using CO_2 as an abundant and renewable carbon source, but also avoiding the use of toxic and environmentally harmful phosgene. Organic carbonates, especially cyclic carbonates, are commercially important, 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. Another important use of a cyclic carbonate, such as propylene carbonate (PC) and ethylene carbonate (EC), is for the formation of dimethyl carbonate (DMC). Industrially DMC could be synthesized from MeOH and PC (or EC), with stoichiometric propylene glycol (PG) or ethylene glycol (EG) as by-products. To avoid wastage of diols and for better utilization of CO_2, it is desirable to develop a process for the synthesis of cyclic carbonate from diol and CO_2.

On the other hand, room temperature ionic liquids (RTILs) have held great promise in the development of green chemical applications and process. For their special physical and chemical properties, such as high thermal stability, negligible vapor pressure, nonflammable, large electrochemical windows and high conductivity, RTILs have been recognized as advantageous alternatives to volatile organic solvents in organic synthesis, catalysis, extraction process, especially in electrochemical applications. It has also been reported that CO_2 is remarkably soluble in imidazolium-based ionic liquids [5-7], which, therefore, makes the reaction of CO_2 in RTILs possible and suitable [8-10].

Even a lot of catalyst systems have been developed for fixation of CO_2, especially to cyclic carbonates, high temperature and high pressure are often needed. The main reason for this is the carbon atom in CO_2 is in its most oxidized form and is therefore relatively unreactive. A large input of energy is required to transform CO_2. Fortunately, electrochemistry is an effective method to activation and utilization of CO_2 at room temperature and normal pressure. Deng et al. [11] reported the electrochemical activation of CO_2 for synthesis of cyclic carbonate from epoxide in IL under mild condition. In our previous studies, we also firstly established electrocarboxylation of activated olefins [12], benzyl chloride [13] and electroactivation of CO_2 with alcohols to synthesis linear organic carbonates [14] in CO_2-saturated RTILs. With our continuous research on the fixation of CO_2 in RTILs, here, we report another new method for synthesis of cyclic carbonates from CO_2 and diols in RTILs under mild condition without catalysts.

2. EXPERIMENTAL

2.1.Reagents

The ionic liquids were used in this paper were prepared as prescribed in the literature [22].1-Methylimidazol was distilled under reduced pressure, sodium tetrafluoroborate 98.0%, sodium hexafluorophosphate 98.0%, acetone 99.5%, dichloromethane 99.5%, diethyl ether 99.7%, 1-bromobutane 98.0%, potassium carbonate 99.0%, magnesium sulphate androus 98.0%, methyl iodide 98.5%, 1,2-propanediol 99.0%, 1,2-butanediol 98.0%, 1,2-pentanediol 98.0%, 2,3-butanediol 97.0%, 1-phenyl-1,2-ethanediol 97.0%, distilled water were used as received.

2.2. Cyclic voltammetry and general electrosynthesis

Cyclic voltammograms were measured with CHI600c electrochemical analyzer in a conventional three-electrode cell. Silver (Ag), copper (Cu) and nickel (Ni) electrodes (d = 2 mm) were used as a working electrode. The counter electrode and reference electrode were a platinum wire and Ag/AgI/0.1 M n-Bu_4NI in DMF, respectively.

Typical potentiostatic electrolysis was carried out by CHI600c in C_4MIMBF_4 containing of 0.1 mol L^{-1} diol under a slow stream of CO_2 in an undivided cell equipped with a magnesium rod sacrificial anode and a metallic ring cathode until 1.0 F of charge was passed. The reaction mixture was esterified directly in C_4MIMBF_4 by adding anhydrous K_2CO_3 and methyl iodide and stirring the mixture at 50 ^oC for 5 h. The solution was extracted with Et_2O, and the organic layers washed with H_2O, dired over $MgSO_4$, and evaporated. The recycle of ionic liquid process is similar as our previous work [12, 13].

The corresponding organic carbonates 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).

Butylene carbonate **2a:** GC-MS (m/z, %) 116 (M^+, 4), 87 (64), 71 (4), 57 (15), 43 (100); ^1H NMR ($CDCl_3$): 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-Pentyl-[1,3] dioxolan-2-one **2c:** GC-MS (m/z, %) 130 (1), 116 (1), 103(3), 87 (24), 71 (33), 58 (57), 43 (100); ^1H NMR ($CDCl_3$): δ 0.91 (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 **2d:** GC-MS (m/z, %) 164 (M^+, 66), 131(1), 119 (15), 105 (32), 90 (100), 78 (71), 65 (19), 51 (25), 39 (13); ^1H NMR ($CDCl_3$): δ 4.36 (t, J=9Hz, 1H), 4.81 (t, J=9Hz, 1H), 5.69 (t, J=8Hz, 1H), 7.27-7.48 (m, 5H).

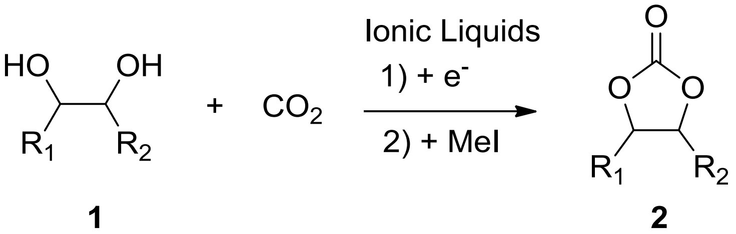
4,5-Dimethyl-[1,3] dioxolan-2-one **2e** GC-MS (m/z, %) 116 (M^+, 3), 101 (4), 86 (1), 73 (3), 57 (7), 51 (2), 43 (100), 38 (6), 28 (78); ^1H NMR ($CDCl_3$): δ 1.46 (q, J=6Hz, 6H), 4.32-4.35 (m, 2H).

3. RESULTS AND DISSCUSION

3.1. Electrosynthesis of butylene carbonate from CO_2 and 1,2-butanediol

The reactivity of diols with electrochemically activated CO_2 in IL was checked by electrosynthesis. To obtain the suitable electrolysis potential, the electroreduction behavior of CO_2 was analyzed by cyclic voltammetry (Fig. 1) firstly.

For comparison, the backgrounds of C_4MIMBF_4 were recorded on Ag, Cu and Ni electrodes (red, --), which show no redox peak in the scan region at 55 ^oC. After saturated with CO_2, an irreversible reduction peak was observed at -1.47 V on Ag electrode, which should be ascribed to the one-electron reduction of CO_2 to generate an anion radical of CO_2 ($CO_2^{\cdot-}$). The similar behavior could be found on both Cu and Ni electrodes, with the peak potential of -1.55 V. Then the potentiostatic electrolysis in CO_2-saturated C_4MIMBF_4 solution containing 1,2-butanediol 1a were carried out on Ag, Cu and Ni electrodes under -1.5 V, -1.6 V, and -1.6 V at 55 ^oC, respectively. After the esterification by MeI, butylene carbonate 2a were obtained (Scheme 1), with the yield of 6 %, 6 % and 7 %, respectively.



(a) $R_1 = Et$, $R_2 = H$; (b) $R_1 = Me$ $R_2 = H$;
(c) $R_1 = n\text{-}C_5H_{11}$, $R_2 = H$; (d) $R_1 = Ph$, $R_2 = H$;
(e) $R_1 = R_2 = Me$

Scheme 1

To optimize the experimental conditions for the electrosynthesis of cyclic carbonates from CO_2 and diols, the influence of various parameters was checked using 1a as a model compound. The results are summarized in Table 1. Series electrolysis were carried out under the potentials from -1.6 V to -1.9 V to investigate the influence of electrolysis potential. As shown in Table 1 (entries 1-4), the highest yield was achieved under -1.7 V. A strong decrease in the yield was observed at more negative potential. It is mainly because that most of the electrons were used to reduce C_4MIMBF_4 rather than CO_2 at negative potential, which could be confirmed by previous CVs. As shown in Fig.1, the cathodic limit of C_4MIMBF_4 is around -1.7 on Ni electrode, after which the current increases significantly.

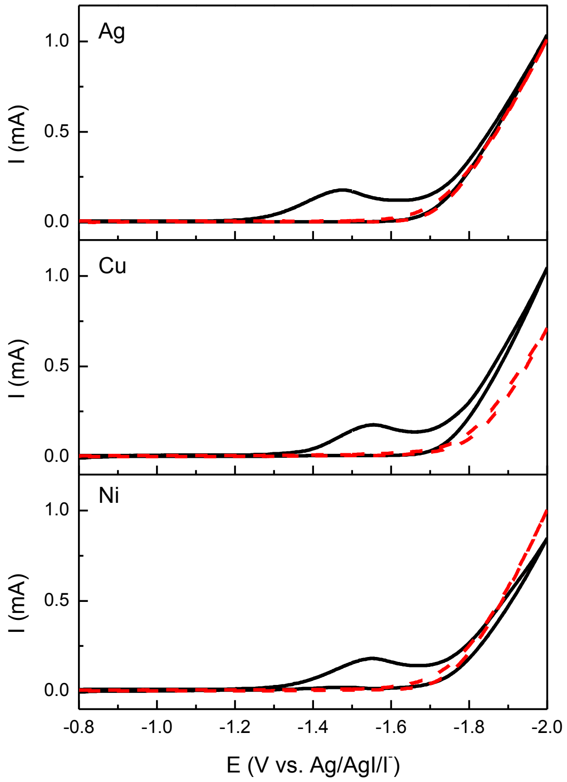


Figure 1. Cyclic voltammograms recorded on Ag, Cu and Ni electrodes in C_4MIMBF_4 saturated with CO_2 (—) and N_2 (--), respectively ($v = 0.1$ V s^{-1}, temperature = 55 °C).

Table 1. Electrosynthesis of butylenes carbonate from 1,2-butanediol and CO_2 in C_4MIMBF_4[a]

Entry	Potential / V	Temperature / ^{o}C	Concentration / mol L^{-1}	Yield [b] / %
1	-1.6	55	0.10	7
2	-1.7	55	0.10	11
3	-1.8	55	0.10	6
4	-1.9	55	0.10	2
5	-1.7	40	0.10	2
6	-1.7	45	0.10	6
7	-1.7	50	0.10	12
8	-1.7	60	0.10	9
9	-1.7	50	0.05	7
10	-1.7	50	0.15	6
11	-1.7	50	0.20	5

a: General condition: Ni cathode, Mg anode, Q = 1.0 F, CO_2 pressure = 1atm. b: GC yield.

Although RTILs has high ionic conductivity, its viscosity is extremely high, which will strongly affect on the rate of mass transport within solution. Therefore, numerous electrosynthesis in RTILs have been carried out at 40-60 ^{o}C [12, 14-19]. High temperature could avail to decrease the viscosity of RTILs and also increase the conductivity, however, it will also decrease the solubility of CO_2 in RTILs. To check the influence of temperature on this reaction, the electrolysis were carried out at 40 to 60 ^{o}C.

The results in Table 1 (entries 2, 5-8) shows that an increase of temperature from 40 to 50 ^{o}C brings a remarkable increase of carbonate yield from 2 to 12 %, while the yield decreased with continuously increase of temperature to 60 ^{o}C. Here the effect of temperature on the CO_2 electroreduction behavior in C_4MIMBF_4 was also examined on Ni electrode at 0.1V s^{-1}. As shown in Fig. 2, upon increasing the temperature, the reduction peak moves to more positive potential, which implies much easier for the reduction. Surprisingly, a small unusual reduction peak was detected on the reverse scan at 50 to 60 ^{o}C.

The large current decay around -1.7 to -1.5 V in the positive-going scan at high temperature may be ascribed to electrode surface poison by the electroreduced mediate from CO_2. Under positive potential, the blocking may be removed from the surface, which causes the current reincrease. This could be used to explain the optimized synthesis condition is 50 ^{o}C rather than much higher temperature. The further investigation about this interesting CV behavior is still going. The influence of diol concentration on the carbonate yield was also investigated from 0.05 mol L^{-1} to 0.2 mol L^{-1}. As shown in Table 1, the highest yield of 12 % was obtained with 1,2-butanediol concentration of 0.10 mol L^{-1}.

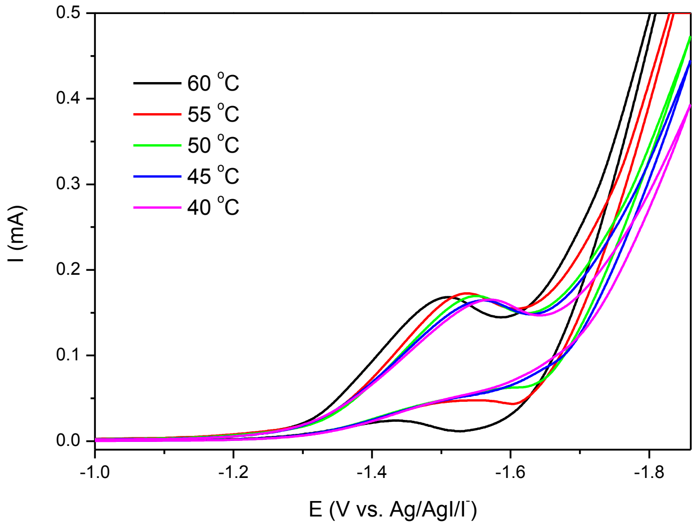


Figure 2. Cyclic voltammograms of CO_2 in $BMIMBF_4$ recorded at v= 0.1 V s^{-1} on Ni electrodes at various temperature: (a) 40 ^{o}C, (b) 45 ^{o}C, (c) 50 ^{o}C, (d) 55 ^{o}C, (a) 60 ^{o}C.

Table 2 summarizes the results of electrosynthesis of 1,2-butanediol in different RTILs, combing with the physical properties. The composition of the RTILs appears to be a crucial factor for the electrochemical reaction of CO_2 and 1,2-butanediol. For C_4MIMPF_6, the viscosity is 2.5 times of that of C_4MIMBF_4, while the conductivity is less than half of that of C_4MIMBF_4, which makes the electrochemical reaction much harder in C_4MIMPF_6. Therefore, even the CO_2 solubility is higher, the carbonate yield is much lower in C_4MIMPF_6. This indicates that the viscosity and conductivity of RTILs is the key factor for electrosynthesis.

Table 2. Electrosynthesis of butylenes carbonate in different ionic liquids

RTLs	Yield ^{a} / %	Viscosity^{b} mPa S	Conductivity^{b} mScm^{-1}	H_{CO2}^{b,c} bar
C_4MIMBF_4	12	33.1 [20]	6.5 [21]	88.9±3.2[7]
C_4MIMPF_6	2	67.1 [20]	3.1 [21]	81.3±0.5[7]

a: Electrosynthesis condition: 0.1 mol L^{-1} 1,2-butanediol – RTILs, Ni cathode, Mg anode, E = -1.7 V, T = 50 ^{o}C, Q = 1.0 F, CO_2 pressure = 1atm. b: Data at 50 ^{o}C. c: Henry's constant for CO_2 dissolved in RTILs.

3.2. Reuse of ionic liquid

One significant benefit for the use of RTILs is recyclable. In this study, C_4MIMBF_4 was separated from the electrolyte system after the previous run, then recovered and reused in the next run. As shown in Fig. 3, the carbonate yield maintained ca. 12 % for 6 cycles, which indicates that the RTIL for this electrosynthesis system is recyclable.

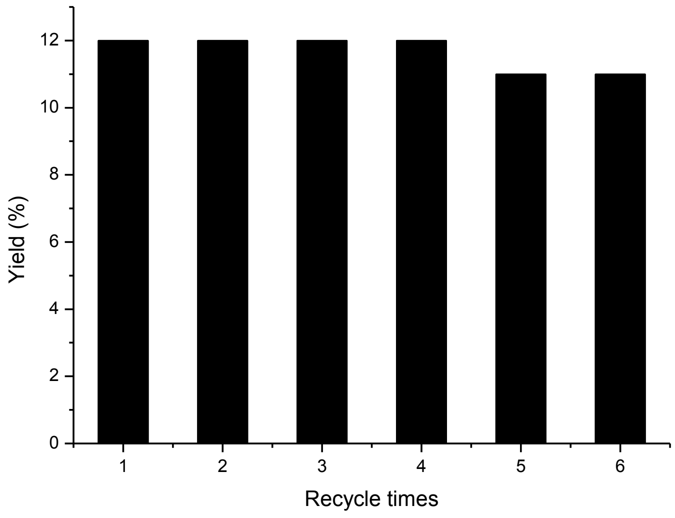
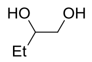
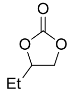
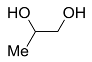
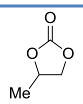
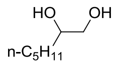
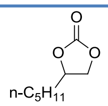
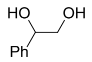
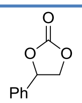
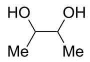
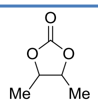


Figure 3. Reuse of C_4MIMBF_4 in the electrosynthesis of butylene carbonate from 1,2-butanediol and CO_2. Reaction conditions as Table 1 entry 7.

3.3. Electrosynthesis of other cyclic carbonates

To test the effectiveness and generality of this methodology, the investigation was extended to other diols.

Table 3. Electrosynthesis of organic carbonates from diols and CO_2 in C_4MIMBF_4[a]

Entry	Substrate	Product	Yield^b / %
1	 1a	 2a	12
2	 1b	 2b	4
3	 1c	 2c	11
4	 1d	 2d	6
5	 1e	 2e	1

a: Electrosynthesis condition: 0.1 M diol – C_4MIMBF_4, Ni cathode, Mg anode, E = -1.7 V, T = 50 ^oC, Q = 1.0 F, CO_2 pressure = 1atm. b: GC yield.

The results of these electrolyses under the previous optimized condition (Table 1, entry 7) are reported in Table 3. When the ethyl group was changed to methyl, the carbonate yield was decreased to 4 % (Table 3, entry 2). Much larger substituent group, such as n-C_5H_{11} and phenyl, will also decrease the carbonate yields to 11 and 6 % (Table 3, entries 3-4). Once both carbon atoms of diol were substituted, such as 1e, a lower carbonate yield of 1 % was obtained (Table 3, entry 5).

3.4. Electrochemical reaction pathway

The interaction of CO_2 and diol was examined by cyclic voltammetry (Fig. 4). When diol was added into C_4MIMBF_4, no reduction peak could be detected in the scan region (Fig. 4 curve b). Even the reverse point was extended to more negative potential (Fig. 4 curve c), only dramatically current increase was observed after -1.6 V, which presents the cathodic limit of the system. It indicates that, in C_4MIMBF_4, diol cannot be electroreduced in the scan region. Compare to pure C_4MIMBF_4, the much larger current is mainly caused by the decrease of viscosity and increase of conductivity for the addition of diol. As described previously, a reduction peak of CO_2 was observed after C_4MIMBF_4 was saturated with CO_2 (Fig. 4 curve d). When the diol was added into C_4MIMBF_4 saturated with CO_2, the reduction peak of CO_2 was moved to more positive potential (Fig. 4 curve e). Meanwhile, on the reverse scan, the reduction current is larger than that without diol and the unusual reduction peak was disappeared. This behavior may be due to the interaction between diol with the electroreduced mediate from CO_2 (Eq. 1), which is blocking the electrode surface without diol. To confirm the key role of $CO_2^{\cdot -}$, an electrolysis was carried out under N_2 in C_4MIMBF_4 containing 1,2-butanediol at previous optimized condition. At the end of the electrolysis, CO_2 was bubbled into the electrolyte and stirred for 1 h. After esterification, no cyclic carbonate was detected.

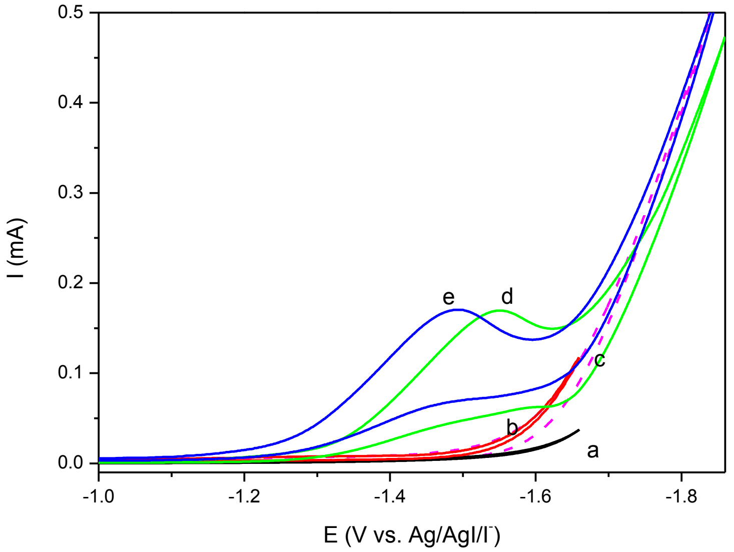
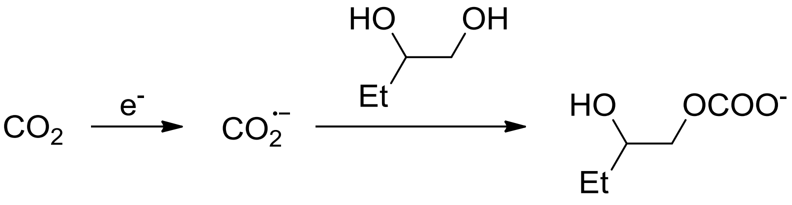


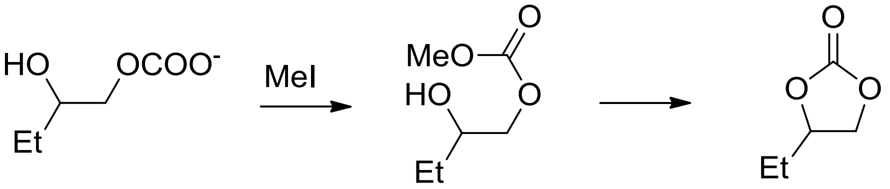
Figure 4. Cyclic voltammograms of CO_2 and 1,2-butanediol in C_4MIMBF_4 recorded at v= 0.1 V s^{-1} on Ni electrodes at 50°C. (a) C_4MIMBF_4, (b-c) C_4MIMBF_4 containing 0.02 mol L^{-1} 1,2-butanediol, (d) as (a) saturated with CO_2, (e) as (b) saturated with CO_2.



3

(1)

The yield comparison between 2a and 2e implies that $CO_2^{\cdot -}$ prefers to react with primary alcohol, rather than secondary alcohol. Therefore, the reaction of $CO_2^{\cdot -}$ with 1,2-butanediol should produce intermediate **3** (Eq. 1). Then during the esterification process, **3** was transferred to linear carbonate **4**, which was turned into cyclic carbonate **5** immediately (Eq. 2). According to literature [23], linear carbonates(2-18%), and cyclic carbonates(18-30%) are present, together with dicarbonates(2-12%) by the way of electrogenerated bases in organic solvent. Comparatively, besides the main product of cyclic carbonate, only trace linear carbonate was detected by GC-MS in our work, while no dicarbonate was obtained. It indiacates that much higher cyclic carbonate selectivity could be achieved by electrosynthesis in RTILs.



3 **4** **5**

(2)

4. CONCLUSIONS

On the basis of the above investigations, electrosynthesis of cyclic carbonates from CO_2 and diols could be achieved by using RTILs as solvent-electrolyte media for the first time. The synthesis was carried out under mild condition (P = 1 atm, T = 50 ^oC) without additional catalysts. The effects of cathode materials, the electrolysis potential, the temperature, diol concentration and ionic liquid type were investigated. For this reaction system, ionic liquid is recyclable. Although the yield was affected significantly by the diol structures, this method is available for all the diols tested.

ACKNOWLEDGEMENTS
This work was financially supported by the Project for the National Natural Science Foundation of China (20973065), Basic Research in Natural Science Issued by Shanghai Municipal Committee of Science, China (08dj1400100), “Chen Guang” project supported by Shanghai Municipal Education Commission and Shanghai Education Development Foundation, China (10CG26), Specialized Research Fund for the Doctoral Program of Higher Education (20100076120020), and the Fundamental Research Funds for the Central Universities, China.

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