

Synthesis of Cyclic Carbonates from CO₂ and Diols via Electrogenenerated *N*-Heterocyclic Carbenes

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Synthesis of cyclic carbonates has been achieved from CO₂ and diols in room temperature ionic liquids (RTILs) via electrogenerated *N*-heterocyclic carbenes with good yields. Only mild reaction conditions of 40 °C temperature and 1 atm CO₂ were used. This work provides a new procedure for synthesis of cyclic carbonates, as well as expands the function of NHCs.

Keywords: Electrogenenerated, *N*-Heterocyclic Carbenes, Cyclic Carbonates, CO₂, Diols

1. INTRODUCTION

Since carbon dioxide is expected to be a ubiquitous and abundant C1 feedstock from industrial wastes, much effort has been made to develop effective processes for desirable, economically competitive products from carbon dioxide.[1] One of the most promising ways that effectively utilizes CO₂ is the synthesis of cyclic carbonates through the coupling reaction with epoxides.[2] 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.[3] Another important use of a cyclic carbonate, such as propylene carbonate (PC) and ethylene carbonate (EC), is for dimethyl carbonate (DMC) formation. It is well known that the transesterification of PC (or EC) with methanol to form DMC is widely used in industrial synthetic process.[4] But in this process stoichiometric propylene glycol (PG) or ethylene glycol (EG) as by-products was obtained. To avoid wastage of diols and for better utilization of CO₂, it is desirable to develop a process for the synthesis of cyclic carbonates from diols and CO₂. Thus utilization of diols and CO₂ for the synthesis of cyclic carbonates becomes a theme of great interest. Numerous homogeneous and heterogeneous catalyst

systems associated with metal complexes,[5] organic bases,[6] metal oxides,[7] have been developed for this transformation. However, the yield of cyclic carbonate was very low which was attributed to the thermodynamic limitation.

N-heterocyclic carbenes (NHCs) are well established as organocatalysts and ligands in organic synthesis[8-11] which could be generated by deprotonation with a suitable base[12, 13] or by a direct single electron cathodic reduction of imidazolium cations.[14-17] With their lone pair of carbene electrons, NHCs behave as nucleophiles. It has been known that nucleophilic NHCs can activate CO₂ to form imidazolium carboxylates (designated as NHC-CO₂ adduct). Recently, NHCs have been employed as CO₂ transformation catalysts[18-24] with epoxides or propargyl alcohols [22, 23] which provide a new approach on the potential use of CO₂ as C1 chemical feed stock for the synthesis of cyclic carbonates. Furthermore imidazolium carboxylates have been acted as a CO₂ delivery agent in the carboxylation of organic compounds with active hydrogen (acetone, cyclohexanone, and benzyliocyanide).[25, 26] Despite these advances, the utility of NHCs in fixation of CO₂ remains sparse. In an effort to increase the function of NHCs, we have investigated the synthesis of cyclic carbonates from CO₂ and diols via electrogenerated NHCs, in which RTILs play the dual roles of green solvents as well as precursors of NHCs.

2. EXPERIMENTAL

2.1. Apparatus and reagents

Voltammetric measurements were conducted using the CHI650C electrochemical station in a conventional three-electrode cell. The working electrode was a glassy carbon disk ($r=1$ mm). The auxiliary electrode was a platinum spiral wire. The reference electrode was Ag/AgI/0.1 M n-Bu₄NI in *N,N'*-dimethylformamide. Galvanostatic electrolysis was performed using a direct current-regulated power supply HY3002D (HYelec®, China). ¹H NMR spectra were recorded on an AVANCE 500 (500 MHz, Bruker, Germany) spectrometer in CDCl₃ with Me₄Si as an internal standard. Mass spectra were obtained using a 5973-N spectrometer connected with an HP 6890 gas chromatograph (Agilent, USA). Diols were used as received (J&K) without further purification. The ionic liquids used were prepared as described in the literature [27].

2.2. General electrochemical procedure

2.2.1. Electrolysis of styrene glycol (**1a**) - BMIMBF₄ (0.4M) in organic solvents followed by bubbling CO₂ under galvanostatic conditions

Catholyte (2 mmol of BMIMBF₄ and 1mmol of **1a** in 5.0 mL of organic solvent) and anolyte (5.0 mL organic solvent - 0.1 M TEABF₄) were separated through cation-exchange membrane. The electrolysis was carried out, under N₂ atmosphere at 40 °C, at constant current ($j=18.9$ mA cm⁻²). After consuming a charge of 2.0 F mol⁻¹, the current was switched off, CO₂ bubbling (instead of N₂) was

started and stirring was performed for 2 h. The electrolyte was then esterified by adding anhydrous K_2CO_3 (1.0 mmol) and MeI (3.0 mmol), and the mixture was stirred at 60 °C for 5 h. After all these reactions, the solution was hydrolyzed and extracted with ethyl ether. And the organic layer, which contains product, was dried with $MgSO_4$ and analyzed by gas chromatography to obtain the yields based on the starting materials.

2.2.2. Electrolysis of solutions of **1a** in $BMIMBF_4$ followed by bubbling CO_2 under galvanostatic conditions

Preparative electrolysis was conducted at 40 °C in a two-compartment cell. A solution of ionic liquid (5 ml) containing **1a** (1.0 mmol) was electrolyzed under galvanostatic control ($j=18.9 \text{ mA cm}^{-2}$) under N_2 . After the consumption of the number of Faradays per mol of **1a** reported in Table 1, the current was switched off, the bubbling of CO_2 (instead of N_2) was started and stirring was performed for 2 h. Then electrolyte was esterified by adding anhydrous K_2CO_3 (1.0 mmol) and MeI (3.0 mmol), and the mixture was stirred at 60 °C for 5 h. After all these reactions, the solution was extracted with ethyl ether. And the organic layer, which contains product, was dried with $MgSO_4$ and analyzed by gas chromatography to obtain the yields based on the starting materials.

The following compounds were prepared according to this procedure.

4-Phenyl-[1,3] dioxolan-2-one 2a 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 (500 MHz, $CDCl_3$): δ 4.36 (t, $J=9\text{Hz}$, 1H), 4.81 (t, $J=9\text{Hz}$, 1H), 5.69 (t, $J=8\text{Hz}$, 1H), 7.27-7.48 (m, 5H).

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

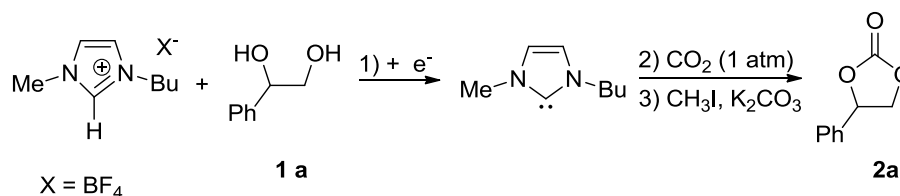
4-propyl-[1,3] dioxolan-2-one 2c GC-MS (m/z, %) 129 (1), 102 (1), 87 (67), 71 (20), 57 (40), 43 (100); 1H NMR (500 MHz, $CDCl_3$): δ 0.99 (t, $J=7\text{Hz}$, 3H), 1.42-1.44 (m, 1H), 1.50-1.53 (m, 1H), 1.66-1.69 (m, 1H), 1.80-1.82 (m, 1H), 4.08 (t, $J=8\text{Hz}$, 1H), 4.54 (t, $J=8\text{Hz}$, 1H), 4.70-4.76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

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

3. RESULTS AND DISCUSSION

3.1. Electrosynthesis of styrene carbonate from CO_2 with styrene glycol

In the preliminary study, styrene glycol (**1a**) was first chosen as a model molecule for the investigation of the electrosynthesis of cyclic carbonate via electrogenerated NHCs (Scheme 1). Experiments have been conducted to investigate the effects of various experimental parameters, such



Scheme 1. Electrosynthesis of styrene carbonate from CO₂ and glycol.

as the nature of the RTIL, cathode materials, charge amounts, current densities, temperatures and stirring times on the yields of target product, the electrolysis results were summarized in Table 1.

To verify the effectiveness of electrogenerated carbenes for the above reaction, firstly, BMIMBF₄ was electrochemical reduced in different organic solvents such as DMF and MeCN (Table 1, entries 1, 2). The electrolysis results showed that **2a** was synthesized successfully from **1a** and CO₂ via electrogenerated NHCs in organic solvents. In order to further illuminate the role of carbenes generated by cathode reduction, the reaction was conducted without electric current passing through the cell in DMF-BMIMBF₄ (Table 1, entry 3); the result showed that the reaction did not take place without electric current.

Table 1. Synthesis of styrene carbonate from CO₂ and **1a** via electrogenerated NHCs in organic solvent-BMIMBF₄ (0.4 M) and ILs ^[a]

Entry	Solvent	Cathode	Q (F mol ⁻¹)	j (mA cm ⁻²)	$T^{[b]}$ (°C)	t (h)	Yield ^[c] (%)
1	DMF	Ti	2.0	18.9	40	2.0	11
2	MeCN	Ti	2.0	18.9	40	2.0	19
3 ^[d]	DMF	-	-	-	40	2.0	0
4	BMIMBF ₄	Ti	2.0	18.9	40	2.0	48
5	PeMIMBF ₄	Ti	2.0	18.9	40	2.0	23
6	BDMIMBF ₄	Ti	2.0	18.9	40	2.0	16
7	BMIMBF ₄	GC	2.0	18.9	40	2.0	12
8	BMIMBF ₄	Ss	2.0	18.9	40	2.0	34
9	BMIMBF ₄	Ni	2.0	18.9	40	2.0	23
10	BMIMBF ₄	Cu	2.0	18.9	40	2.0	35
11	BMIMBF ₄	Pt	2.0	18.9	40	2.0	30
12	BMIMBF ₄	Ti	1.0	18.9	40	2.0	47
13	BMIMBF ₄	Ti	1.5	18.9	40	2.0	60
14	BMIMBF ₄	Ti	1.5	13.9	40	2.0	25
15	BMIMBF ₄	Ti	1.5	16.7	40	2.0	35
16	BMIMBF ₄	Ti	1.5	21.1	40	2.0	53
17	BMIMBF ₄	Ti	1.5	18.9	30	2.0	37
18	BMIMBF ₄	Ti	1.5	18.9	50	2.0	48
19	BMIMBF ₄	Ti	1.5	18.9	60	2.0	40
20	BMIMBF ₄	Ti	1.5	18.9	40	0.5	45
21	BMIMBF ₄	Ti	1.5	18.9	40	1.0	51
22	BMIMBF ₄	Ti	1.5	18.9	40	1.5	56
23	BMIMBF ₄	Ti	1.5	18.9	40	2.5	62

^[a] Electrolysis carried out in divided cell, styrene glycol = 0.2 mol/L, P_{CO₂} = 1atm; ^[b] Temperature of electrolysis and stirring; ^[c] GC yield based on **1a**; ^[d] Without electric current passing through the cell.

Having assessed the validity of electrogenerated carbenes in cyclic carbonate **2a** synthesis, the classical organic solvent was removed, and RTIL was used as medium as well as NHC precursor. Moreover, ionic liquids are electrically conducting fluids, and the use of a supporting electrolyte is not necessary. To evaluate the general efficiency of RTILs as NHCs precursors and solvents, RTILs with different cations such as BMIMBF₄ and PeMIMBF₄ were employed in the procedure (Table 1, entries 4, 5). Both of these two 1,3-dialkylimidazolium ionic liquids were found to be good precursors of NHCs and solvents, but better yield of **2a** was obtained employing BMIMBF₄ (Table 1, entry 4), which mainly because lower viscosity and higher conductivity of BMIMBF₄.

To complete this study, electrolysis was performed on 1-butyl-2, 3-methyl-imidazolium tetrafluoroborate which cannot generate carbene in the C2-position. Unexpectedly **2a** was obtained although with low yield (BDMIMBF₄, Table 1, entry 6). This phenomenon can be attributed to the acidic methyl in the 2-position [28], which can be cathodically deprotonated with low current efficiency. Thus, the reactivity of an electrogenerated NHC is affected by the RTIL itself.

The nature of cathode materials has great influence on the yield or reactivity in the electrochemical process. Therefore, a set of electrolysis were performed at different cathodes (Table 1, entries 4, 7-11). The results showed that the yield of **2a** decreased depending on the employed cathode material in the following order: Ti (48%) > Cu (35%) > Stainless steel (34%) > Pt (30%) > Ni (23%) > GC (12%).

The yields of **2a** were affected by the charge passed in electrolyses Q (i. e., by the number of equivalents of electrogenerated carbene; Table 1, entries 4, 12, 13). As the presence of the non-Faradaic current, the Faradaic efficiency cannot achieve 100%. Consequently more over the theoretic charge is usually needed to improve the yield. The best yield of 60% was obtained when the passed charge reached 1.5 F mol⁻¹ (Table 1, entry 13). Before the point of 1.5 F mol⁻¹, the yield increased rapidly with the increase of the passed charge. After then, the yield was decreased to 48% for 2.0 F mol⁻¹, which may attribute to side reactions of imidazolium cations. [14]

The yields of **2a** were also affected by current density (Table 1, entries 12-15). In fact, both low and high current densities led to lower yields with respect to the optimum value of 60% at 18.9 mA cm⁻² (Table 1, entry 13). The results obtained at low current densities can probably be ascribed to a longer electrolysis time, which can lead to side reactions such as dimerization and dealkylation of imidazolium cations at the cathode after reduction to imidazol-2-ylidenes [14]. The results at high current densities can be ascribed to a lower current efficiency with the increased ohmic component. The best result was obtained using 18.9 mA cm⁻² current density (Table 1, entry 13).

The temperature can be a crucial factor for this reaction. High temperatures decrease RTIL viscosities and increase the conductivity[29], as well as affect the solubility of CO₂. Therefore the effects of the reaction temperature were examined (Table 1, entries 13, 17-19). Increased the temperature from 30 °C to 40 °C favored the reaction, but further increased temperature resulted in lower yield of **2a**. The best yield of target product was achieved at 40 °C.









Extremely high RTIL viscosities strongly affect the rate of mass transport within a solution. Low-rate mass transport may result in long reaction time to get a satisfactory value. Thus, the effects of the stirring time (Table 1, entries 13, 20-23) were examined. The best result was achieved at $t = 2.5$

h (Table 1, entry 23). In fact after 2 h, the stirring time was slightly effective for improving the yield of **2a**.

3.2. Electrosynthesis of cyclic carbonates from other diols

To examine the effectiveness and generality of the proposed electrochemical methodology, the investigation was extended to other diols for which one of the two carbon atoms bearing the hydroxyl group was primary, while the other was secondary (**1b**, **1c**), or both of the two carbon atoms bearing the hydroxyl group was secondary (**1d**). The reactions were carried out under the conditions reported for Table 1, entry 13. The results of analyses are reported in Table 2 and some conclusion could be drawn. In all case, diols (**1b-1d**) reacted with CO₂ in the presence of NHCs to afford cyclic carbonates with good yields except for **1d**.

Table 2. Synthesis of cyclic carbonates via electrogenerated NHCs according to the conditions (Table 1, entry 13)

Entry	Substrate	Product	Yield (%)
1	 1a	 2a	60
2	 1b	 2b	63
3	 1c	 2c	61
4	 1d	 2d	17

3.3. Electrochemical reaction pathway

To understand the reaction pathway, the electrochemical behaviours of BMIMBF₄ and reactants were investigated by cyclic voltammetry (CV). To check the electrochemical behaviour of BMIMBF₄, DMF was used as the solvent for the CV study. As shown in Fig. 1, there were no redox peaks in the scan region before addition of BMIMBF₄ under N₂ (curve a). After addition of 26 mM of BMIMBF₄, a single reduction peak at -2.1 V was observed during the forward scan which was ascribed to imidazolium cation reduction. During the following scan reversal, a significant oxidation peak appeared at 0.05 V corresponding to the oxidation of new electroactive species generated from imidazolium cation reduction. In order to testify the peak at 0.05 V belongs to 1,3-dialkylimidazolium-2-ylidene oxidation, here we measured the oxidation of 1,3-dialkylimidazolium-2-ylidene (inset in Fig. 1, curve e) generated by heating NHCs-CO₂. The inset in Fig. 1 showed that the oxidation peak potential of 1,3-dialkylimidazolium-2-ylidene is -0.054V which is similar with that of generated by

BMIMBF₄ reduction. These observations prompted to presume that the electroreduction of BMIMBF₄ produces the carbene.

To check the reactants' behaviour, **1a** (10 mM) was added into the solution of DMF-TEABF₄ (0.1 M). As shown in Fig. 1 curve c, there is no obvious peak of reduction or oxidation, which indicates that **1a** cannot be reduced or oxidized under the experimental conditions.

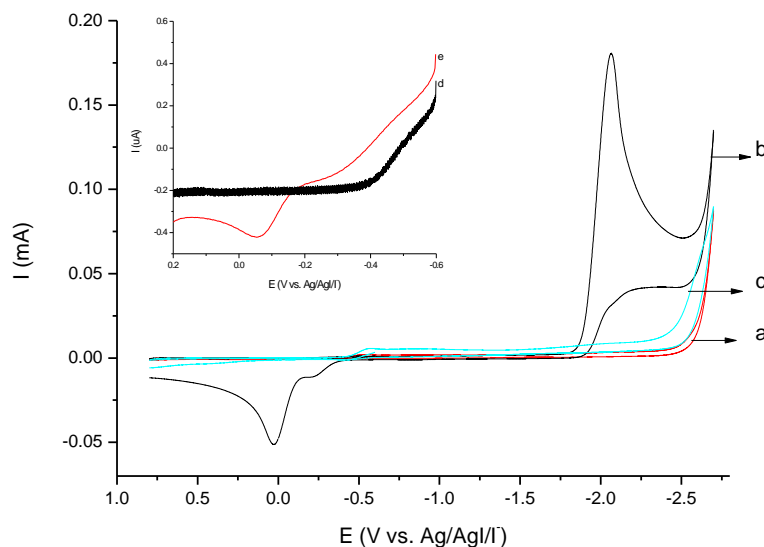


Figure 1. Cyclic voltammogram of a DMF-TEABF₄ (0.1 M) solution at 100 mVs⁻¹ on GC electrode (a) without BMIMBF₄, (b) contains 26 mM BMIMBF₄, (c) as (a) contains 10 mM **1a**. The inset shows the electrochemical behaviour of (d) NHCs-CO₂ (20 mM) in the solution of DMF-TEABF₄ (0.2 M), (e) as (d) heated at 90 °C for 8h.

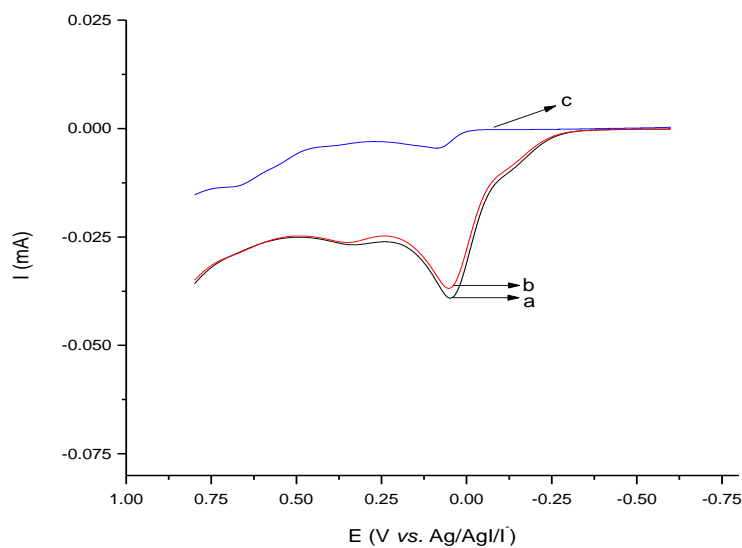
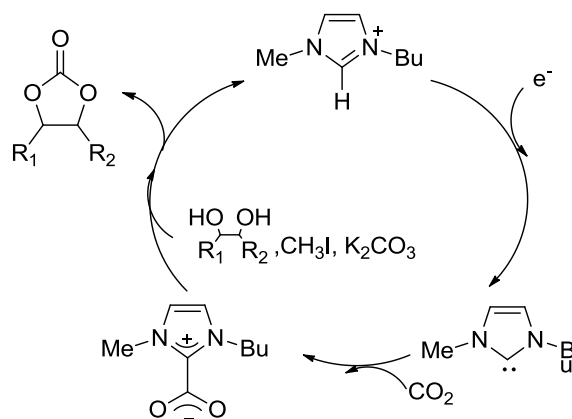


Figure 2. Linear sweep voltammograms of NHC generated by cathodic reduction of DMF-BMIMBF₄ (0.2M) solution kept under the atmosphere of (c) N₂ for 0 min, (d) N₂ for 5 min, (e) CO₂ for 5 min.

NHCs could freely react with CO_2 to form the corresponding carboxylates which have been suggested by many authors, but the progress of the addition reaction supported by electrochemical analysis has not been reported. To check the progress, linear sweep voltammogram (LSV) of the reaction had been studied. Firstly to get NHCs, electrolyse BMIMBF_4 (0.2M) in DMF under galvanostatic control had been done. After the consumption of 96.4 C charge, the current was switched off. The electrolyte was scanned by LSV which was shown in Fig.2 (curve a). After kept stirring under the atmosphere of N_2 for 5min, the oxidation peak current reduced slightly (Fig.2, curve b). While after bubbling of CO_2 instead of N_2 for 5 min, the oxidation peak current decreased sharply (Fig.2, curve c). It indicates that CO_2 reaction with NHCs to afford NHC-CO_2 resulted in free NHCs with decreased electroactive. Consequently, the peak current of oxidation also decreased.

It is known, in fact, that 1-butyl-3-methyl-1H-imidazol-2-ylidene is a singlet carbene and behaves mainly as a nucleophile and a base. Chiarotto et al reported that 1-butyl-3-methyl-1H-imidazol-2-ylidene can be indicated as the base involved in the deprotonation of the chiral oxolidin-2-ones. [30] To further understand our reaction mechanism, we had done an experiment to exclude the possibility of deprotonation of **1a**. Electrolyzed the solution of **1a** (0.2M)- BMIMBF_4 (5 mL) under N_2 atmosphere, after consuming 2.0 F mol^{-1} of charge, the current was switched off. The electrolyze solution was divided into two parts. One part was added CH_3I and refluxed for 5h, the other was extracted by diethyl ether directly. Workup the experiments and detected them by GC-MS. The results showed that no product was gotten converted from **1a**. If a deprotonation of **1a** by the NHCs took place, added CH_3I into electrolyzed solution, 2-methoxy-1-phenylethanol would be easy to form [31]. But, no 2-methoxy-1-phenylethanol was formed. So the mechanism of deprotonation of **1a** can be ruled out.

Based on CVs' study and our experimental results, we speculate that NHCs generated by cathodic reduction reacts with CO_2 to afford NHC-CO_2 , then NHC-CO_2 transfers CO_2 to diols to produce the corresponding cyclic carbonates in the presence of CH_3I and K_2CO_3 (Scheme 2). By the way, as for how NHC-CO_2 reaction with diols is not very clear at this moment which needs for further investigation.



Scheme 2. Plausible mechanism of synthesis cyclic carbonates via electrogenerated NHCs.

4. CONCLUSIONS

Synthesis of cyclic carbonates has been achieved under mild conditions and shown to give good yields in RTILs via electrogenerated NHCs. The dual role of RTILs as green solvent and NHC precursor avoided the use of organic solvents and the addition of supporting electrolytes.

Electrosynthesis of cyclic carbonates via cathodic reduction of RTILs was affected by cathode materials, charge amounts, current densities, temperatures and stirring times as well as the nature of the RTILs. Moreover, the plausible mechanism had been proposed.

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