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Electrochemical Synthesis of Dimethyl Carbonate with Carbon Dioxide in 1-Butyl-3-Methylimidazoliumtetrafluoborate on Indium Electrode

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Electrochemical reduction of carbon dioxide on indium (In) electrode to synthesis dimethyl carbonate was studied in ionic liquid, 1-butyl-3-methylimidazoliumtetrafluoborate ($BMIMBF_4$). The electrochemical behavior of electrocatalytic reduction CO_2 on In electrode in ionic liquid $BMIMBF_4$, had been studied by cyclic voltammogram with a reduction peak at -1.8 V (vs. Ag). The electrolysis experiments were carried out by constant-potential electrolysis in an undivided cell under mild conditions without any toxic solvents, catalysts and supporting electrolytes, affording the dimethyl carbonate in a moderate yield (76%) at a potential of -1.7 V (vs Ag). The results showed that the yields were affected by temperature, working potential and charge passed.

Keywords:

1. INTRODUCTION

With the rapid development of technology and economy, carbon dioxide (CO_2) becomes one of the main gases leading to the green house effect, and the increasing amount of CO_2 has caused many environmental problems [1]. However, CO_2 is recognized to be a naturally abundant, nontoxic and recyclable carbon source that can sometimes replace toxic chemicals, such as phosgene and cyanide, carbon monoxide [2]. Thus, the conversion and utilization of CO_2 becomes more and more significant from the ecological and economic point of view.

Dialkyl carbonates are an important class of compounds. Their versatility allows their application in several fields of chemical and pharmaceutical industry [3]. Dimethyl carbonate(DMC), as an environmentally building block, can be used as carbonylating reagents, fuel additives, alkylating reagents and polar solvents [3] to replace toxic reagents like phosgene, dimethyl sulfate. Therefore, synthesis of DMC should been extensively studied.

Electrochemical fixation of CO_2 was considered to be an effective route of chemical fixation. Synthesis carbonates from the electrochemical reduction of CO_2 in methanol and some aprotic solvents have been investigated extensively [4-8]. However, the use of supporting electrolyte and toxic organic solvents makes it more complex to recover the solvents. Moreover, it could not meet the demands of environmental friendly technologies.

Ionic liquids, with wide electrochemical potential window, high ionic conductivity, good solvating ability and low vapour pressure, have been used as green reaction media in organic synthesis [9]. A number of investigations have shown that CO_2 is remarkably soluble in imidazolium-based ionic liquids [10]. Recently, some groups have reported electrochemical fixation of CO_2 in ionic liquids to obtain valuable carboxylated products [11-15]. Various electrode materials have been researched, including semiconductors, supramolecular and metal cathodes. Indium, as a kind of metal with good conductivity, can act actively in CO_2 reduction, no matter in aqueous solution or nonaqueous media, and carbonate ion were a main product in nonaqueous media [16].

So, it is expected that introducing the indium electrode for the electrochemical reduction of CO_2 in ionic would result in an improvement of the yield. Herein, we began to study the reduction of CO_2 on Indium electrode in ionic liquid 1-butyl-3-methylimidazolium- tetrafluoborate($BMIMBF_4$) in DMC synthesis.

2. EXPERIMENTAL

2.1. Chemicals

The ionic liquid $BMIMBF_4$ (with a purity of more than 99%) was dried under vacuum at 110 °C until cyclic voltammetric results indicated that there was no detectable water, as the presence of water would narrow the electrochemical potential window of the ionic liquid $BMIMBF_4$ [14,17]. The purity of CO_2 and argon (Ar) was 99.99%. Unless otherwise noted, the reagents and solvents were used as received from commercial suppliers.

2.2. Typical electroanalytical and electrolysis procedure

The electroanalytical experiments were carried out using CHI660B electrochemical station (Shanghai Chenhua Instrument Company) in an undivided cell, with indium electrode (In, area=1 cm^2) as the working electrode, platinum (Pt, area=1 cm^2) foil as the counter electrode and silver (Ag) wire as the reference electrode. Prior to the experiments, all electrodes were polished mechanically and then were sonicated (KQ-50DE) in ethanol for 5 min to remove any microparticulates. Finally, all the electrodes were cleaned with diluted hydrochloric acid and double distilled water and then were dried with Ar gas.

The electrolysis experiments were conducted in a standard undivided glass cell equipped with In electrode (area=1cm^2) and a magnesium rod (Mg, d = 0.5 cm) sacrificial anode. The potentiostatic electrolysis was carried out using CHI660B electrochemical station with three electrodes. Prior to each test, $BMIMBF_4$ (4 mL) was bubbled with CO_2 for 30 min to be saturated. Then a suitable constant potential was applied and continuous CO_2 flow was maintained throughout the duration of the whole electrolysis experiment. After a certain amount of charge (Q) had been supplied to the electrode, the electrolysis was interrupted. Then methanol (CH_3OH) was added, and stirred for 1h. Finally, CH_3I (3-fold excess) was added as an alkylation agent and the mixture was stirred at 55 °C for 6 h.

Gas chromatography–massspectra (GC–MS) was recorded with HP6890/5973 GC–MS an Agilent 1100 series.

Dimethyl carbonate: MS (m/z, %): 90 (M+, 8), 75(1), 60(9), 59(77), 45(100), 33(8), 31(47), 29(36), 28(8), 15(37).

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammetry of CO_2 on Indium in $BMIMBF_4$

Cyclic voltammograms (CV) of CO_2 in $BMIMBF_4$ on indium electrode were recorded at the scan rate of 50 mVs^{-1} in an undivided cell at 25 °C with Pt foil as counter electrode and an Ag wire as reference electrode. As can be seen from Fig. 1a, after bubbling Ar gas for 20 min, there was no reduction peak in the sweeping region from -1.3 V to -2.3 V in neat $BMIMBF_4$. It should be noted that the cathodic current began to increase at around -2.1 V, due to the reduction of $BMIMBF_4$ [13,14]. As shown in Fig. 1b, in CO_2-saturated $BMIMBF_4$, a single irreversible reduction peak is observed at -1.8V (vs. Ag), which is attributed to the reduction of CO_2 to $CO_2^{\bullet -}$.

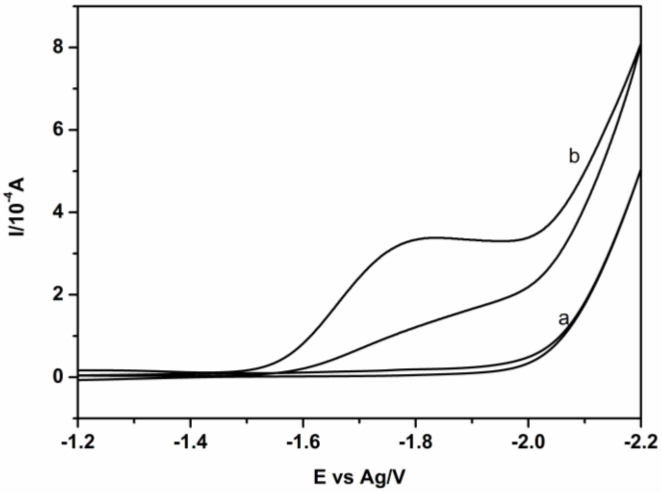

Figure 1. Cyclic voltammograms recorded with In electrode at the scan rate of 50 mVs^{-1} at 25 °C: (a) neat $BMIMBF_4$, (b) $BMIMBF_4$ saturated with CO_2.

The effect of the scan rate on the CV behavior of CO_2 on In electrode in $BMIMBF_4$ was examined at 25 °C, the results are presented in Fig. 2. The reduction peak shifted toward negative potential, and the cathodic peak current enhanced with increasing the scan rate from 20 to 100 mVs^{-1}. The peak current varies linearly with $v^{1/2}$, indicating that the electrode process is controlled by diffusion rather than adsorption [18-21].

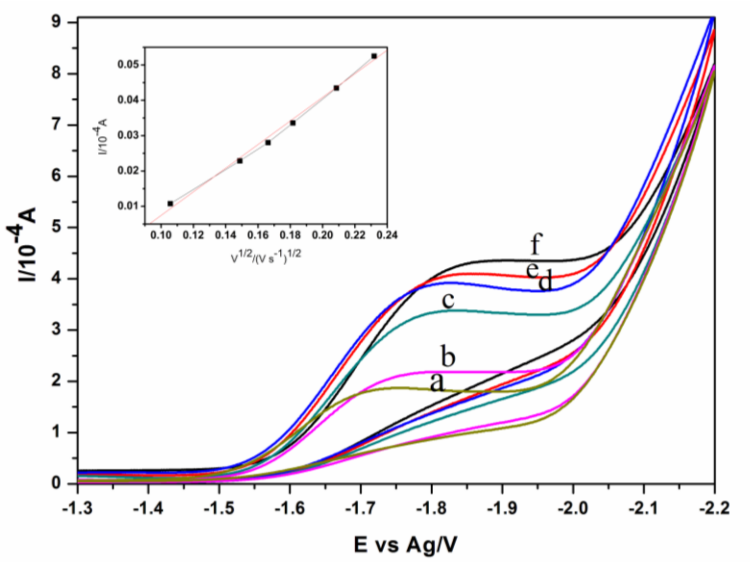

Figure 2. Cyclic voltammograms of CO_2 in $BMIMBF_4$ at 25 °C on In electrode at various scan rates:(a) v=20 mVs^{-1}, (b)40 mV^{-1}, (c)50 mV^{-1}, (d) 60 mV^{-1}, (e) 80 mV^{-1}, and (f) 100 mV^{-1}.

3.2. Influence of reaction conditions

In order to optimize experimental conditions, the influence of temperature, working potential and charge passed on the yield of DMC was investigated under constant voltage condition. In addition, potentiostatic electrolysis was performed under optimized conditions. All experimental results were summarized in Table 1. The yields were calculated on the CH_3OH.

3.2.1. Effect of temperature

Temperature plays an important role in this electrochemical reduction reaction, because the viscosity of ionic liquids is very high, affecting on the rate of mass transport within solution [9,13]. Electrolysis experiments were carried out under constant potential from 30 °C to 70 °C. The results of Table 1 (entries 1-5) show that the optimized yield are obtained at 40°C, which can reach to 76%. The yields of DMC decrease remarkable with the increase of the temperature from 40 °C to 70 °C. In addition, the yield is hardly changed from 60 °C to 70°C.

It is widely known that the viscosity of $BMIMBF_4$ displays an essential Arrhenius behavior [9]. Increase temperature can decrease the viscosity of ionic liquid, and then lead to an increase of conductivity , which is helpful to this reaction. But lower temperature is favorable to increase of solubility of CO_2 in $BMIMBF_4$ [9,13]. Due to the above factors, the optimal temperature was chosen as 40 °C.

3.2.2. Influence of working potential

As shown in table 1 (entries 6-9), different yield of DMC were found at the end of the electrosynthesis at different working potentials, appreciable differences in the yield of DMC were found. The values of -1.5, -1.7, -1.9, -2.1 V were chosen as electrosynthesis potentials. The influence of electrolysis potential was studied at a charge consumption of 1 F mol^{-1}. The relationship between electrosynthesis potentials at and yields of DMC was listed in table 1. According to the experimental results, the yield of DMC decreased with the increasing potential. The optimized potential for this electrosynthesis in $BMIMBF_4$ is -1.7 V.

3.2.3. Influence of charge passed

The charge passed (Q) supplied to the electrodes during the reduction of CO_2 to $CO_2^{\bullet -}$ has a great influence on the yield of DMC. The experiments were investigated under a potential of -1.7 V at 40 °C. As shown in table 1(9-11), it had a higher value of 76% at 1.0 F mol^{-1}. When the amount of electrogenerated $CO_2^{\bullet -}$ was equal to that of alcohol, the best yield was achieved. Before that point, the yield was rapidly increased, because the concentration of $CO_2^{\bullet -}$ in $BMIMBF_4$ increased with increasing the charge consumption. After that point, superabundant $CO_2^{\bullet -}$ will favour the reaction where $CO_2^{\bullet -}$ reacted itself [22] resulting in yield decrease.

Table 1. Reaction conditions and results of electrosynthesis of dimethyl carbonate in $BMIMBF_4$

Entry	Temperature (°C)	Potential (V) vs. Ag	Q(F mol^{-1})	Yield (%)
1	30	-1.7	1.0	71
2	40	-1.7	1.0	76
3	50	-1.7	1.0	69
4	60	-1.7	1.0	32
5	70	-1.7	1.0	35
6	40	-1.5	1.0	53
7	40	-1.9	1.0	67
8	40	-2.1	1.0	51
9	40	-1.7	0.6	60
10	40	-1.7	1.0	76
11	40	-1.7	1.4	52

Therefore, the optimized condition for the electrosynthesis of DMC from CO_2 in $BMIMBF_4$ on In electrode was under a charge consumption of 1.0 F mol^{-1} with a potential of -1.7 V at 40 °C.

3.3. Mechanism of electrosynthesis of DMC in BMIMBF$_4$

Based on our experimental results and work of other's [13], the proposed pathway is outlined in Fig. 3 and Fig. 4. Initially an CO_2 molecule approaches and comes into contact with In electrode surface. The CO_2 molecule is then activated by weak adsorption of In electrode surface and the $CO_2^{\bullet\,-}$ is formed. Then the $CO_2^{\bullet}\,{}^{-}BMIM^{+}$ ion-pairing was existed, and quickly formed $CH_3OCOO^{\bullet\,-}$ with methanol. When and the solution was stirred at 55 °C for 6 h after alkylation agent CH_3I was added, DMC come out to be synthesised.

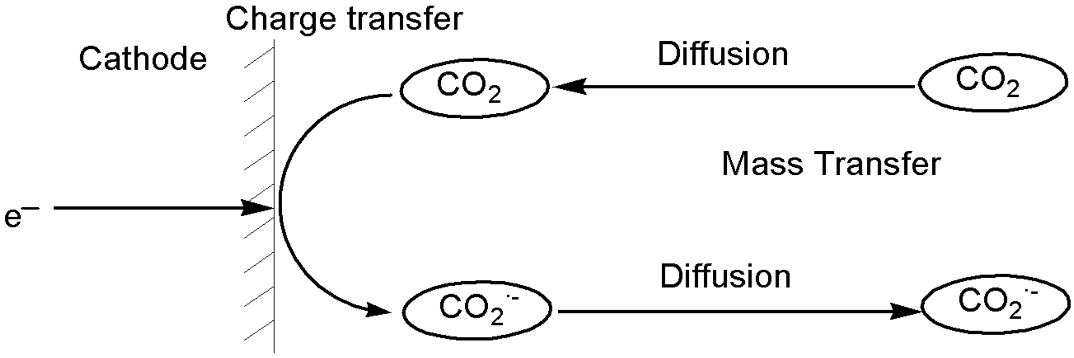

Figure 3. The proposed pathway of CO_2 electroreduction in $BMIMBF_4$

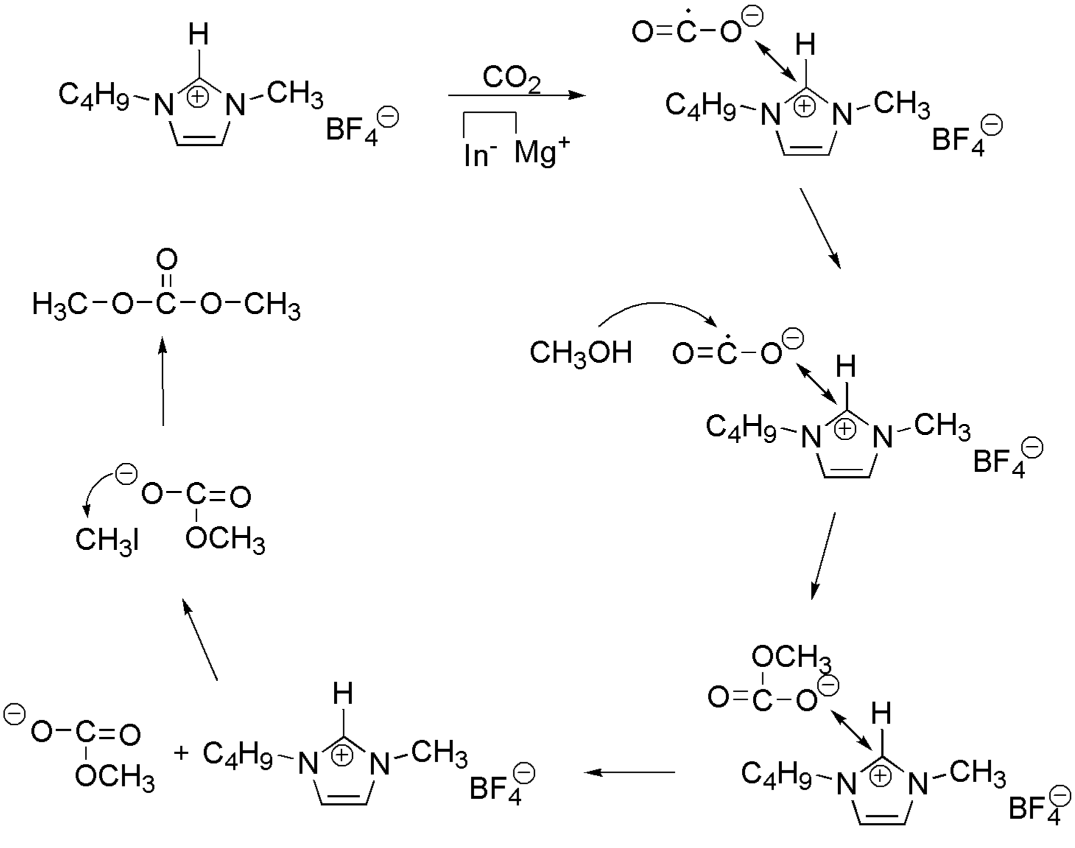

Figure 4. The proposed pathway DMC formed in $BMIMBF_4$

4. CONCLUSIONS

Cyclic voltammetry showed that Indium could act as a good catalytic electrode for the electroreduction of CO_2 in $BMIMBF_4$.The electrolysis experiments were carried out in an undivided cell under mild conditions, avoid the addition of toxic solvents and catalysts. Cyclic voltammetry of CO_2 in $BMIMBF_4$ on In electrode shows that there is an obvious peak current of CO_2 reduction at -1.8 V. The influence of temperature, working potential, charge passed on the yields was investigated, and the target product could be obtained in moderate to good yields under optimized condition. Moreover, the best yield of 76% appears at a temperature of 40 °C, which is much lower than other materials mentioned in literature [13]. Efforts are under way to explore more electrochemical carboxylation systems for the electrochemical fixation of CO_2 aimed at "greenchemistry".

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