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Electrochemical Reduction Behaviour of CO_2 on Cu Electrode in Ionic Liquid ($BMIMBF_4$) During Synthesis of Dimethyl Carbonate

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The electrochemical reduction behaviour of CO_2 on Cu electrode in ionic liquid, 1-butyl-3-methyllimidazolium tetrafluoborate ($BMIMBF_4$), during the synthesis of dimethyl carbonate was studied. The experiments were carried out in three electrodes undivided cell under mild conditions and the use of volatile solvents and catalysts, as well as any other additional supporting electrolytes, was avoided. The electrochemical reduction behaviour of CO_2 on Cu electrode in $BMIMBF_4$ had been studied by cyclic voltammetry with a reduction peak at -1.9 V (*vs*. $Ag^+/AgCl$) and the reduction process was mostly controlled by diffusion. Dimethyl carbonate was obtained in 73.2 % faradaic efficiency, under the optimized condition.

Key Words: Electrochemical reduction, CO_2, Ionic liquid, Dimethyl carbonate.

INTRODUCTION

Carbon dioxide is the most important greenhouse gas. Its concentration in the earth's atmosphere has risen by more than 30 % since industrial revolution[1]. Excessive CO_2 is causing the average temperatures of the world's oceans to elevate, which will lead to catastrophic events, such as iceberg to melt, more drought to occur. Therefore great effort has been placed toward the reduction of CO_2. In addition, CO_2 can be proposed as a safe and abundant source of carbon in synthesis organic compounds[2].

One of the most promising utilization of CO_2 is synthesis of dimethyl carbonate (DMC). Since dimethyl carbonate can be used as environmentfriendly intermediate for organic synthesis replacing poisonous phosgene and dimethyl sulfate. It is also considered as an option for meeting the oxygenate specifications on gasoline[3]. Synthesis of dimethyl carbonate has been paid to considerable attention since late 1970s. Several attractive methods had been reported[3-9]. Some reactions had been performed in the presence of organmetallic complexes[4,5], inorganic bases[6] and modified ZrO_2[7]. Those methods were complex but conversion was very low. Recently, there were a few reports on the one-pot synthesis of dimethyl carbonate, but supercritical conditions were required during the reaction[8,9]. Therefore, it has been desired to develop new methods for synthesis of dimethyl carbonate.

Under this condition, electrochemical reduction of CO_2 in ionic liquids arouses a strong interest in many researchers[10-12]. Electrochemistry techniques can provide preliminary activation of CO_2, which is required in the synthetic process. Ionic liquids have held great promise in the development of green chemical applications and processes. Their nonvolatility, exceptional solubility of CO_2, high conductivity, wide electrochemical windows and ability to act as catalysts, make them can be used as "Green" media in clean organic synthetic processes as substitutes for conventional toxic and volatile solvents.

It had been reported that carbonates[10] and carbamates[11,12] were obtained by reduction of CO_2 in ionic liquid $BMIMBF_4$. Those researches focused on looking for efficient and benign methods for synthesis of organic compounds, however, the kinetic characteristics and mechanism of the reduction process were rarely mentioned. Otherwise the electrochemical reactions often occur on the interface between electrode and electrolyte, the material of electrode can facilitate or hinder a desired electrochemical reaction[13]. Previous work had shown that CO_2 reduction had been studied on different electrode materials and Cu electrode had the high electrocatalysts to this reaction[14]. Keeping this in mind, we studied kinetic characteristics and mechanism of the reduction process on Cu electrode in $BMIMBF_4$ by means of cyclic voltammogram and potentiostatic electrolysis. The effects of the potential on faradaic efficiency were also evaluated.

EXPERIMENTAL

The purity of CO_2 and argon (Ar) were 99.99 %. The ionic liquid $BMIMBF_4$ (with a purity of more than 99 %) was dried under vacuum at 120 ºC, until cyclic voltammogram indicated that there was no detectable water. Methanol was dried by distillation from metallic magnesium (Mg) power. CH_3I was dried over 4 A molecular sieves.

Electroanalytical procedure: Electroanalytical measurements were performed in a standard three electrodes undivided cell in $BMIMBF_4$, with Cu foil as the working electrode (area = 0.5 cm^2), Pt foil (area = 1 cm^2) as the counter electrode and Ag^+/AgCl as the reference electrode. All potentials are given with respect to this reference electrode.

Electrochemical reduction of CO_2 synthesis of dimethyl carbonate: Potentiostatic electrolyses were performed in an undivided cell with a gas inlet and outline. The electrolytic solution was $BMIMBF_4$ (5 mL). A ringed Cu electrode was used as the working electrode (area = 5 cm^2), Mg rod (d = 0.5 cm) was used as the counter electrode and Ag^+/AgCl as the reference electrode. The Mg rod was placed down the middle of the ringed Cu cathode. Prior to every experiment, the solution was bubbled with CO_2 under stirring for 0.5 h to be saturated. After that the electrolyses were performed at a constant potential at 55 ºC, until 1 F of charge passed. Continuous CO_2 flow was maintained throughout the duration of the whole electrolyse process. At the end of electrolyse, CH_3OH (0.03 mL) was added, stirred for 1.0 h. Finally, 5 fold molar CH_3I (0.2 mL) was added, stirred at 55 ºC for 5 h. The reaction mixture was distilled to obtain product. 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).

RESULTS AND DISCUSSION

Cyclic voltammograms: Cyclic voltammograms on Cu electrode in $BMIMBF_4$ were measured at 25 ºC. Fig. 1 shows the typical curves. As can be seen from Fig. 1a, there was no reduction peak was observed in sweeping region -1.3 V ~ -2.6 V. It also can be observed that the cathodic current started to increase at around -2.2 V, which was due to the reduction of the $BMIMBF_4$.

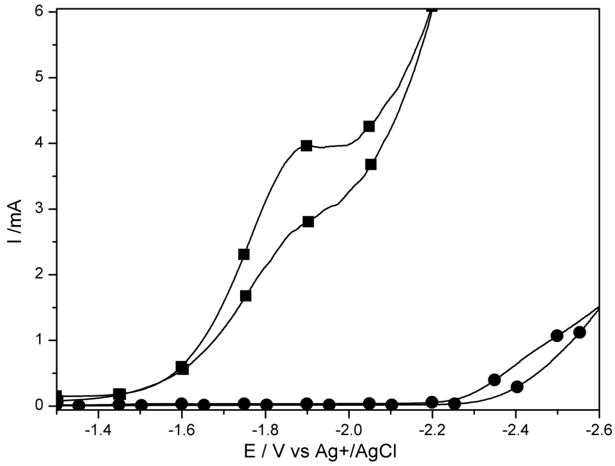

Fig. 1. Voltammograms on Cu electrode recorded at 10 mV s^{-1} in $BMIMBF_4$ after bubbling Ar (a) and after bubbling CO_2 (b)

After the solution was saturated with CO_2, the cathodic current started to increase at around -1.5 V (Fig.1b) and a distinct reduction peak appeared at about -1.9 V, that should result from the reduction of CO_2. On the other hand, in this potential region, there were no oxidation peaks during the reaction process, which indicated the CO_2 reduction process was irreversible, which is due to the formation of the CO_2^{-} and $BMIM^+$ complex.

Effect of temperature on the electrochemical reduction of CO_2: The viscosity of ionic liquids is very high, which will strongly affect on the rate of mass transport within solution[15-17]. So the effect of temperature on the reaction was investigated firstly. In order to identify the reaction mechanism, the effect of temperature was studied from 25-75 ºC under steady state conditions, for which cyclic voltammograms were recorded at 10 mV s^{-1}. Fig. 2 shows plots of log (j) *versus* log (T^{-1}).

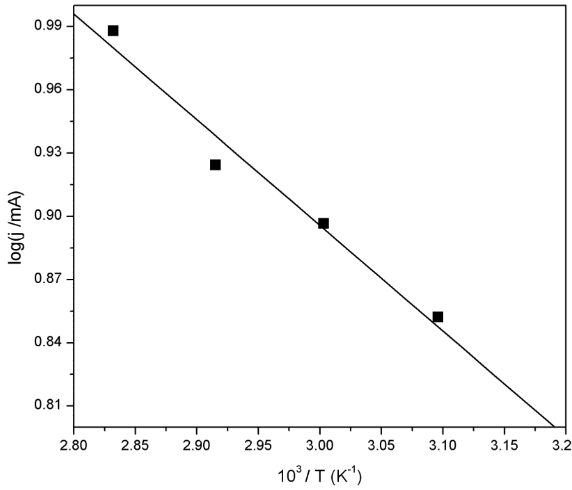

Fig. 2. Plots of log (j) *versus* T^{-1} for electroreduction of CO_2-saturated $BMIMBF_4$ on Cu electrode

The corresponding activation energy (ΔH^*) is estimated by using the following equation[18]:

$$\left[\frac{\partial \log j_p}{\partial\left(\frac{1}{T}\right)Ep,c}\right] = -\frac{\Delta H *}{2.3R}$$

where j_P is the peak current density measured at the peak potential (E_P = -1.9 V); R is the universal gas constant, the value is 8.314. The ΔH^* was 10 kJ mol^{-1} (*i.e.*, lower than 50 kJ mol^{-1}) is typical of a diffusion process[19]. Moreover, two cyclic voltammograms were recorded with and without magnetically stirring the electro-lytic solution in order to support the previous statement. Fig. 3 suggests that the non superimposition of the j-E polarization curves is probably caused by a mass transfer control.

Fig. 2 also shows the increase in temperature involved an enhancement of the current densities. It is well known that kinetic viscosity of $BMIMBF_4$ display essentially Arrhenius behaviour[20]. At higher temperature, the viscosity of ionic liquid decreases and CO_2 diffuses faster, leading to the increase of peak currents. Higher temperature is favorable to decrease viscosity of ionic liquid; simultaneously to decrease the solubility of CO_2 which also causes voltammetric and preparative electrolysis currents to be low. Combing the two reasons, the favourable temperature range for this reaction was 55 ºC.

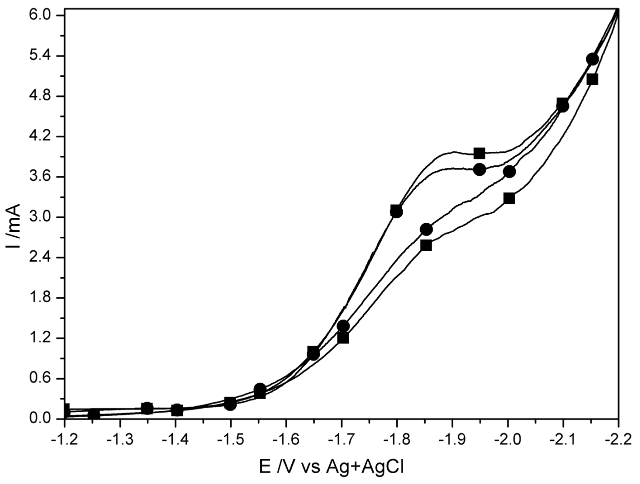

Fig. 3. Voltammograms on Cu electrode recorded at 10 mV s^{-1} in $BMIMBF_4$ after bubbling CO_2 without (a) and with (b) magnetical stirring

To gain more insight into rate-determining step of CO_2 electroreduction, cyclic voltammogram experiments were performed at various potential sweep rates at 55 ºC. Fig. 4 represents the dependence of log (j) on log (v): j is the peak current density and was measured at the peak potential $E_P = -1.9$ V; v is the potential sweep rate (10, 20, 100, 200, 500 mV s^{-1}).

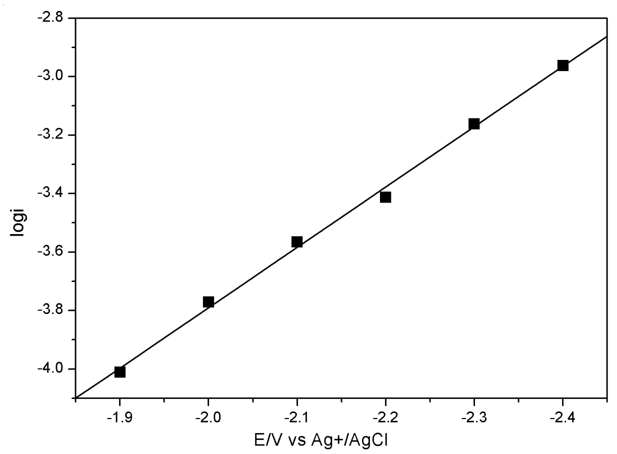

Fig. 4. Plots of log (j) *versus* T^{-1} for electroreduction of CO_2-saturated $BMIMBF_4$ on Cu electrode

In terms of kinetics the mechanism is not pure from, as the slope deviates appreciably from the limiting theoretical value of either 1 (for a pure adsorption process) or 0.5 (for a pure diffusion process)[20-22]. As a result, the slope value of the log (j) *versus* log (v) straight line suggests complicated kinetics involving parallel or successive reactions.

Effect of potential on the Faradaic efficiency: In this work, electrochemical reduction of CO_2 was investigated on Cu electrode $BMIMBF_4$ at 55 ºC. Since the initial step of CO_2 reduction began at negative than-1.5 V, the applied potential range was from -1.6 V to -2.3 V.

The results dealing with the effect of the potential on the Faradaic efficiencies are shown in Table-1. Table-1 shows that the faradaic efficiency of dimethyl carbonate decreased from 72.3 to 15.9 % with the potential became negative. The maximum efficiency of dimethyl carbonate was 72.3 % at -1.9 V. This efficiency was higher compared with that in aqueous solution.

Azuma investigated the electrochemical reduction of CO_2 on Cu electrode in a 50 mmol/dm^{-3} $KHCO_3$ aqueous solution at 20 ºC and obtained methane, ethylene and ethane with Faradaic efficiencies of 17.8, 12.7 and 0.039 %, respectively[23]. Kyriacou and Anagnostopoulos[24] described that the formation efficiencies in the CO_2 electrochemical reduction on Cu at 25 ºC were as follows: for methane 16 %; for ethylene 14 % in 500 mmol/dm^{-3} $KHCO_3$ solution; for CH_4 15 %; for C_2H_4 13 % in 500 mmol/dm^{-3} $CsHCO_3$ solution. Moreover, Yang *et al.*[10] reported that the maximum current efficiency in the CO_2 electrochemical reduction synthesis cyclic carbonates on Cu at 25 ºC was 87 %.

Electrochemical reaction potentials need to be at a certain range, generally speaking, the greater the electrolysis potential, the greater the electrode reaction rate and the shorter the electrolysis time. Because this reaction is a reduction reaction, the more positive is the electrolysis potential, the smaller electrolysis current. When the electrolysis potential was positive than -1.9 V and that didn't reach the required potential electrolysis, this was no electrochemical reduction reaction occur. But when the potential was more negative than -2.2 V, the $BMIMBF_4$ itself polarization is simultaneous to CO_2 reduction, the applied energy is wasted on $BMIM^+$ reduction instead of being used for the reduction of CO_2. Therefore, the suppression of $BMIMBF_4$ reduction is very important. Hence it was found that the most suitable potential for this reaction was -1.9-2.2 V.

Recycle of ionic liquid: Following extraction by ether, dichloromethane (CH_2Cl_2, 20 mL) was added to $BMIMBF_4$. Then the solvent was washed with 1 mL deionized water six times. The obtained aqueous solution was tested with silver nitrate until no precipitate formed, indicating that no chloride ion was present. Then organic layer containing $BMIMBF_4$ was evaporated to remove the CH_2Cl_2. And the obtained $BMIMBF_4$ was dried under vacuum. The recycled $BMIMBF_4$ can be used 3 cycles without activity loss.

TABLE-1
FARADAIC EFFICIENCIES OF DIMETHYL CARBONATE FOR CO_2 REDUCTION AT 55 ºC USING Cu ELECTRODES AT DIFFERENT POTENTIALS

Entry	Potential	Current (mA)	Charge (C)	Faradaic efficiency (%)	Yield (%)
1	-1.8	0.9	59.66	0	0
2	-1.9	2.0	58.95	72.3	72.3
3	-2.0	3.5	60.52	65.1	65.1
4	-2.1	4.6	59.30	60.3	60.3
5	-2.2	5.6	57.88	40.8	40.8
6	-2.3	9.0	59.86	15.9	15.9

Conclusion

The electrochemical reduction of CO_2 on Cu electrode in $BMIMBF_4$ was studied by cyclic voltammogram and potentiostatic electrolysis analysis. The overall kinetics investigated by cyclic voltammogram converged on an electrode process that was mostly controlled by diffusion. The competition between the reduction of CO_2 and the polarization of $BMIMBF_4$ and the Faradaic efficiency of dimethyl carbonate strongly depends on the electrode potential. Optimal results 72.3 % was obtained at -1.9 V. Otherwise, the temperature of the electrolyte also has a great effect on this reaction. Since $BMIMBF_4$ is widely used industrially as a CO_2 absorbent, this research may contribute to applications in the conversion of CO_2 into useful products. Thus, the synthesis of organic compounds by the electrochemical reduction of CO_2 might be of practical interest in medical production as well as production of intermediate materials for the chemical industry.

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