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Short communication

Highly selective and stable electro-catalytic system with ionic liquids for the reduction of carbon dioxide to carbon monoxide

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ABSTRACT

In this study, the electrochemical reduction of CO_2 was examined using a Ag-modified Cu catalyst cathode in a series of mixed ionic liquids (ILs) in the presence or absence of cobalt chloride ($CoCl_2$). These results indicate that the Ag-modified Cu electrode in $EMIMBF_4 + BMIMNO_3$ with $CoCl_2$ exhibited the excellent synergy for the electrochemical reduction of CO_2 to CO with a stable area specific activity, with continuous production for at least 150 h. In such a system, a CO selectivity of 98% was achieved. According to the obtained results, a possible mechanism was proposed. The synergistic effect between the Ag-modified Cu electrode, serving as the main catalyst, and $CoCl_2$ and ILs, serving as the co-catalysts, is probably responsible for the highly selective and stable electrocatalytic reduction of CO_2 to CO.

1. Introduction

The electro-catalytic reduction of carbon dioxide (CO_2) has attracted significant interest, [1] although the conversion of CO_2 to CO or fuels might be unlikely as a technology and has a long way to go to reach the final goal. Owing to a stronger electrostatic field, peculiar micro-environment, and the existence of multi-weak interactions, ionic liquids (ILs) can modulate the activity and selectivity of catalytic reactions. When ILs are used as co-catalysts and reaction media, they decrease the potential for the formation of the intermediates such as carbon dioxide radical anions ($CO_2^{\bullet -}$). For these reasons, researchers have been devoting increasing attention to the electrochemical reduction of CO_2 using ILs [2–9] in the past few years. In particular, Asadi et al. have reported that molybdenum disulfide, as compared to noble metals, exhibits superior performance for CO_2 reduction with a high current density and low overpotential (54 mV) in aqueous 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIMBF_4$) for 10 h.

Meanwhile, silver (Ag) is a promising candidate as an electrocatalyst for the reduction of CO_2, because it can reduce CO_2 to CO with good selectivity, however, it is significantly more expensive than other metal catalysts such as copper (Cu) and iron. To reduce cost and enhance performance, recent studies have been devoted to the development of nanostructured Ag electrocatalysts. For example, Rosen et al. [3] have reported the use of Ag nanoparticles as an electrocatalyst in IL electrolytes, and Salehi-Khojin et al. [10] have studied the influence of Ag nanoparticles on particle size. Furthermore, Lu et al. [11] have employed a nanoporous Ag electrocatalyst, and Kenis et al. [12] have observed a CO selectivity of >90% over a Ag/titania catalyst with a mass activity as high as $2700\ mA \cdot mg_{Ag}^{-1} \cdot cm^{-2}$. In our previous study [7], we have reported that the use of a polycrystalline Ag cathode in BMImCl with 20 wt.% water exhibits excellent synergy for the electrochemical reduction of CO_2 to CO with extremely high selectivity (>99%). However, for large-scale processes, it is essential to develop CO_2 reduction systems based on Ag electrocatalysts with a significantly higher activity. Thus far, various studies have reported the use of Cu electrodes and cobalt (Co) complexes as catalysts for CO_2 electroreduction in various electrolytes [13]. Inspired by previous studies, herein, we developed a system combining Co and a Cu catalyst cathode modified with in situ electrodeposited Ag for CO_2 reduction in ILs.

In this study, the electrochemical reduction of CO_2 was examined using a Ag-modified Cu catalyst cathode in a series of mixed ILs in the presence or absence of cobalt chloride ($CoCl_2$). A highly selective and stable electrocatalytic system for CO_2 reduction was achieved, and a possible mechanism was proposed for this process.

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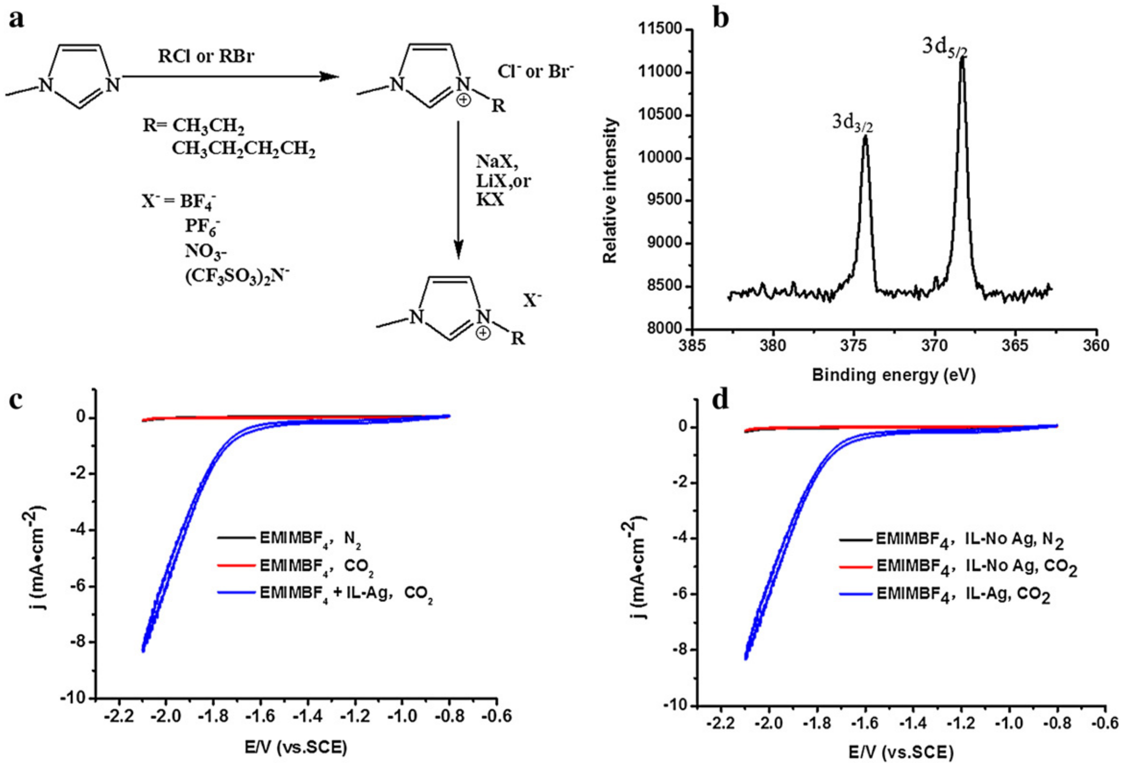

Fig. 1. (a) Synthesis of different ionic liquids; (b) XPS spectrum of Ag on the Cu electrode after CPE for CO_2 reduction; (c) CV traces recorded for the Cu electrode in only 24 g $EMIMBF_4$ under N_2 (black trace); and in 24 g $EMIMBF_4$ under CO_2 (red trace); CV traces recorded for the Ag modified Cu electrode in 24 g $EMIMBF_4$ + 1 g IL–Ag under CO_2 (blue trace); (d) CV traces recorded for the Cu electrode in 24 g $EMIMBF_4$ + 1 g IL–No Ag under N_2 (black trace); in 24 g $EMIMBF_4$ + 1 g IL–No Ag + $CoCl_2$ under CO_2 (red trace); CV traces recorded for the Ag modified Cu electrode in 24 g $EMIMBF_4$ + 1 g IL–A under CO_2 (blue trace).

2. Experimental

Fig. 1 shows a series of ILs with different cation and anion structures, i.e., $EMImBF_4$, $BMImBF_4$, $BMImPF_6$, $EMIMNTf_2$ and $BMImNO_3$; these ILs were synthesized according to literature procedures with slight modification [14]. $AgNO_3$ (2 ppm) in a $BMIMNO_3$ solution was prepared and labeled as IL–Ag, and $BMIMNO_3$ without $AgNO_3$ was labeled as IL–No–Ag. All the ILs were dried under a vacuum at 80 °C for 24 h to reduce the water contents to <500 ppm prior to use. Cyclic voltammetry (CV) measurements were performed on CHI 660A electrochemical workstation system with a conventional three electrode cell at a scan rate of 100 $mV \cdot s^{-1}$.

The modified Cu catalyst cathode with Ag was prepared by the in situ electrodeposition of Ag in an undivided electrolytic cell. The electrolytes were composed of 24 g tested IL, 1 g IL–Ag or IL–No–Ag, in the presence or absence of 0.25 mg $CoCl_2$. The Ag^+ and $CoCl_2$ contents on the Cu electrode or in the electrolyte were measured by inductively coupled plasma–atomic emission spectroscopy (ICP—AES). The electrode surface was analyzed by X-ray photoelectron spectroscopy (XPS). Fig.1b shows the characterized results.

The Cu, Pt wire and saturated calomel electrode (SCE) were used as the working, counter, and reference electrode, respectively. All experiments were performed at 25 °C under atmospheric pressure. Controlled potential electrolysis (CPE) experiments were conducted in the tested electrolyte under a slow stream of CO_2 (20 $mL \cdot min^{-1}$) in the undivided electrolytic cell equipped with a tested cathode (areas approximately 1 cm^2), platinum anode, and SCE. The reaction system was subjected to stability tests at −2.0 or −1.9 V in different ILs using the CPE device. The gaseous products were detected by gas chromatography (GC) using a thermal conductivity. After the completion of electrolysis, the liquid products were extracted using ethyl acetate and were detected by GC(6890)–MS(5973) or HPLC (1200 series).

3. Results and discussion

First, CV was conducted to examine the reduction of CO_2 over Cu in pure $EMImBF_4$ saturated with either CO_2 or N_2 (Fig. 1c). As can be seen by the polarization curves, no obvious was observed in CO_2-saturated $EMImBF_4$ (red trace) as compared to N_2-saturated $EMImBF_4$ (black trace), suggesting that the Cu electrode in $EMIMBF_4$ does not exhibit any activity for the reduction of CO_2. As 1 g of IL–Ag was added to CO_2-saturated $EMIMBF_4$, as shown in blue trace, a dramatic change in the I/V curve was observed after 10 min of electrolysis; in particular, at the onset of reduction, the current density significantly increased at −1.7 V. To identify the electrocatalytic response corresponding to the conversion of CO_2 to a reduced product, CPE experiments were performed in a CO_2-saturated 24 g $EMIMBF_4$ + 1 g IL–Ag using a Cu electrode. After 30 min, GC analysis indicated >99% CO and the formation of trace H_2 as the gaseous product at −1.9 V during electrolysis. Moreover, the composition did not change with increasing negative potential, indicating that the selectivity for CO is not sensitive to potential. After 12 h, CPE was discontinued. The formation of other possible liquid products such as formic acid and methanol was not detected. Moreover, by the ICP–AES results, the Ag content on the Cu electrode was 1.8 $\mu g \cdot cm^{-2}$; However, no Ag was detected in the mixed ILs after CPE, implying that most of the Ag in IL–Ag is electrodeposited on the Cu electrode surface via in situ electrodeposition. Further experiments demonstrated that the observed electrocatalysis cannot be attributed solely to the reduction of CO_2 mediated by $BMIMNO_3$. If the observed electrocatalysis were mediated solely to $BMIMNO_3$, similar results should be obtained in the presence of IL–No–Ag instead of IL–Ag. Unlike those obtained using IL–Ag (Fig. 1d, blue trace), CV traces (Fig. 1d, red trace) for CO_2-saturated $EMIMBF_4$ containing 1 g IL–No–Ag with the Cu electrode virtually showed no enhancement in the current upon scanning to negative potentials as compared to N_2 atmosphere (black