Carbon Dioxide Reduction

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Efficient Reduction of CO_2 into Formic Acid on a Lead or Tin Electrode using an Ionic Liquid Catholyte Mixture

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Abstract: *Highly efficient electrochemical reduction of CO_2 into value-added chemicals using cheap and easily prepared electrodes is environmentally and economically compelling. The first work on the electrocatalytic reduction of CO_2 in ternary electrolytes containing ionic liquid, organic solvent, and H_2O is described. Addition of a small amount of H_2O to an ionic liquid/acetonitrile electrolyte mixture significantly enhanced the efficiency of the electrochemical reduction of CO_2 into formic acid (HCOOH) on a Pb or Sn electrode, and the efficiency was extremely high using an ionic liquid/acetonitrile/H_2O ternary mixture. The partial current density for HCOOH reached 37.6 $mA\,cm^{-2}$ at a Faradaic efficiency of 91.6 %, which is much higher than all values reported to date for this reaction, including those using homogeneous and noble metal electrocatalysts. The reasons for such high efficiency were investigated using controlled experiments.*

Carbon dioxide (CO_2) is the most significant greenhouse gas. It is also a cheap, non-toxic, and abundant C1-feedstock.[1] Compared with thermal and photochemical reactions, electrochemical reduction is a simple approach to convert CO_2 into useful products under mild conditions, which provides opportunities for large-scale practical application.[2] Formic acid (HCOOH) is a very important chemical and can serve as a precursor for value-added chemicals and feedstocks for fuels.[3] There have been many reports on electrocatalysis for CO_2 reduction into HCOOH (Supporting Information, Table S1).[4] Some composite materials such as Ir pincer catalyst immobilized on carbon nanotubes,[4a] noble metal nanoparticles,[4b] and metal oxides[4c,d] have been employed as electrodes coupled with different electrolytes. Although some cheap transition metals, such as Pb and Sn, have been used as electrodes for reduction of CO_2, it is very difficult to achieve a satisfactory CO_2 conversion rate and high selectivity for the desired products simultaneously.[5]

Ionic liquids (ILs), a promising new class of environmentally benign solvents, have attracted extensive interest owing to their unique properties.[6] In particular, their negligible vapor pressure, high ionic conductivity, and wide electrochemical windows make them excellent alternatives for conventional electrolytes in electrochemical applications,[7] including supercapacitors, lithium-ion batteries, and dye-sensitized solar cells. For the electrochemical reduction of CO_2, high CO_2 capture ability and wide potential windows make ILs very attractive electrolytes in catalysis.[8,9]

Many investigations have been conducted into electrochemical reduction of CO_2 in the presence of IL-containing electrolyte. For example, a Ag electrode was used to reduce CO_2 into CO with overpotentials below 0.2 V and a Faradaic efficiency greater than 96 % in a 1-ethyl-3-methylimidazolium tetrafluoroborate ($[Emim]BF_4$)/H_2O mixture.[10] The IL acted as a homogeneous catalyst that improved the catalytic reduction rate of CO_2. High Faradaic efficiency was achieved when CO_2 reduction was performed on carbon nanofibers[11] and MoS_2[12] in a $[Emim]BF_4$/H_2O mixture. The reduction of CO_2 was also performed by employing IL/acetonitrile (AcN)[13] or IL/AcN/tetraalkylammonium hexafluorophosphate ($TBAPF_6$) mixtures[14] as an electrolyte, where the small amount of IL present acted as a supporting electrolyte for the bismuth electrode co-catalyst. A 1-ethyl-3-methylimidazolium trifluoroacetate ([Emim]TFA)/D_2O binary mixture was applied to promote the electrocatalytic reduction of CO_2 into HCOOH on an In electrode with a Faradaic efficiency of 90 %.[5a] CO was generated when a Pb electrode and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[Emim]Tf_2N$)/AcN binary electrolyte was used.[5b] A strongly basic tetraalkyl phosphonium IL, the trihexyltetradecylphosphonium 1,2,4-triazolide ($[P_{66614}]$[124Triz]), was also used as solvent for the reduction of CO_2 into formate at low overpotentials.[15] It is known that the efficiency of an electrochemical reduction process depends strongly on the electrolyte and electrode. In general, cheap transition metal electrodes exhibit a lower current density compared with precious metal electrodes.

Although electrochemical reduction of CO_2 into HCOOH has been studied extensively, it is very difficult to achieve satisfactory current density and Faradaic efficiency of HCOOH (efficiency of charge transferred for HCOOH production in the CO_2 reduction) simultaneously, especially using the electrodes made of cheap and abundant materials. Herein, we describe the first work on electrochemical reduction of CO_2 using ternary mixtures consisting of an IL supporting electrolyte and binary solvents. Interestingly, it was found that 1-butyl-3-methylimidazolium hexafluorophosphate ($[Bmim]PF_6$)/AcN/H_2O or 1-butyl-3-methylimidazolium tetrafluoroborate ($[Bmim]BF_4$)/AcN/H_2O ternary electrolytes were extremely efficient in the electrochemical reaction when using economical Pb or Sn as the cathode.

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The partial current density reached 37.6 mA cm^{-2} at a Faradaic efficiency of 91.6 %, which was much higher than all the values reported in the literature up to date, including those using noble metal electrodes.

The advantages of the ternary electrolyte were verified by a kinetic study using CO_2 saturated pure [Bmim]PF_6, [Bmim]PF_6 (30 wt %)/AcN, and [Bmim]PF_6 (30 wt %)/AcN-H_2O (5 wt %). Herein, the amount of H_2O is calculated on the basis of AcN. The CV curves using Pb and Sn electrodes are shown in Figures 1 A,B, respectively. As shown, the current density in [Bmim]PF_6 (30 wt %)/AcN-H_2O (5 wt %) was much higher than that in [Bmim]PF_6 and [Bmim]PF_6 (30 wt %)/AcN. The CV curves using Pb and Sn electrodes in N_2 saturated [Bmim]PF_6 (30 wt %)/AcN-H_2O (5 wt %) electrolyte were also determined, demonstrating much lower current densities, and thereby indicating the reduction of CO_2.

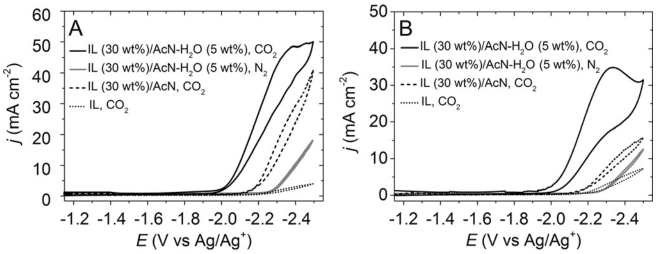

Figure 1. The electrocatalytic performance of Pb and Sn electrodes in various electrolytes containing IL [Bmim]PF_6. CV traces recorded using A) Pb and B) Sn electrodes in various CO_2 or N_2 saturated electrolytes at room temperature.

In response to the results shown in Figure 1, we carried out CO_2 reduction in various ternary IL (30 wt %)/AcN-H_2O (5 wt %) electrolytes on Pb and Sn electrodes. The electrolysis experiments were performed in a typical H-type cell (Supporting Information, Figure S1). After electrolysis at a controlled potential of −2.2 V (vs. Ag/Ag$^+$) for a desired time, the gaseous and liquid products were quantified (see Table 1). Generally, most of the ternary IL/AcN/H_2O mixtures yielded high partial current densities and high selectivities for HCOOH. The imidazolium cation likely helps to lower the activation energy for the CO_2 reduction process.[8] However, the anion played a significant role in the observed catalytic selectivity. The two commonly used ILs [Bmim]PF_6 and [Bmim]BF_4 (entries 1, 2) exhibited much higher current densities and Faradaic efficiencies, which results partially from the strong interaction between CO_2 and fluorine containing ILs.[16] Catholyte containing [Bmim]PF_6 (entry 1) exhibited the highest current density and Faradaic efficiency for HCOOH. In contrast, the ILs without fluorine, such as 1-butyl-3-methylimidazolium nitrate ([Bmim]NO_3) and 1-butyl-3-methylimidazolium dihydrogen phosphate ([Bmim]H_2PO_4), yielded lower current densities and/or lower Faradaic efficiency of HCOOH. Moreover, for ILs that did not contain fluorine the structure of the counter-anions also affected the current density and Faradaic efficiency significantly (entries 5–9). This observation indicates that anions play an important role in the electrochemical reduction of CO_2, which results (in part) from differences in the interactions between CO_2 and ILs with different anions.[17]

The effect of [Bmim]PF_6 content in the ternary mixture [Bmim]PF_6/AcN-H_2O (5 wt %) on the CO_2 reduction activity and the product selectivity was investigated using Pb and Sn electrodes at −2.2 V (vs. Ag/Ag$^+$; Supporting Information, Figure S2). The CV curves on the Pb electrode are illustrated in Figure S3 (Supporting Information), which shows that the current density decreases with increasing IL content in the [Bmim]PF_6/AcN-H_2O (5 wt %) mixture. Figure S2 (Supporting Information) demonstrates that the current density increased dramatically with up to 10 wt % IL content because the IL acted as a supporting electrolyte. Above 30 wt % IL content, current density decreased because of enhanced electrostatic attraction between the anions and cations of the IL, which hinder the motion of the ions and reduce the charge transfer rate. Herein, the by-products were mainly CO with a small amount of H_2. In the IL dominated electrolyte the dominant product switched to CO. That is, the target product can be easily modulated by controlling the solvent-ratio of the catholyte. Although other researchers have reported that the composition of electrolytes affects the selectivity of electrochemical reduction of CO_2,[18] the

Table 1: The partial current density and Faradaic efficiencies of HCOOH (FE_{HCOOH}) on Pb and Sn electrodes at an applied potential of −2.2 V (vs. Ag/Ag$^+$) in IL (30 wt%)/AcN-H_2O (5 wt%) mixtures.[a]

Entry	IL	Pb				Sn			
		j_{HCOOH} [mA cm^{-2}]	FE_{HCOOH} [%]	FE_{CO} [%]	FE_{H2} [%]	j_{HCOOH} [mA cm^{-2}]	FE_{HCOOH} [%]	FE_{CO} [%]	FE_{H2} [%]
1	[Bmim]PF_6	17.0	95.3 ± 1.6	3.0 ± 0.3	1.6 ± 0.1	15.0	95.0 ± 1.7	2.8 ± 0.3	2.0 ± 0.2
2	[Bmim]BF_4	13.4	95.1 ± 2.0	3.2 ± 0.2	1.5 ± 0.1	12.8	94.3 ± 2.0	2.8 ± 0.5	2.5 ± 0.2
3	[Bmim]OTF	12.3	94.6 ± 2.5	2.8 ± 0.2	2.5 ± 0.2	12.5	94.0 ± 2.1	3.2 ± 0.4	2.8 ± 0.3
4	[Bmim]TFA	11.2	92.1 ± 4.0	2.0 ± 0.1	5.8 ± 0.5	10.3	91.7 ± 3.8	3.0 ± 0.3	5.1 ± 0.6
5	[Bmim]ClO_4	12.8	82.0 ± 3.5	2.5 ± 0.4	15.1 ± 0.7	10.1	83.5 ± 5.0	4.2 ± 0.5	12.0 ± 1.7
6	[Bmim]DCA	4.0	76.4 ± 6.0	4.0 ± 0.2	19.5 ± 1.2	4.0	78.6 ± 4.5	3.8 ± 0.5	17.4 ± 2.0
7	[Bmim]SCN	4.6	75.9 ± 6.5	3.5 ± 0.9	20.3 ± 3.2	4.1	76.0 ± 5.0	3.5 ± 0.2	20.0 ± 1.5
8	[Bmim]NO_3	3.5	37.3 ± 7.0	2.1 ± 0.2	60.5 ± 6.0	2.7	26.5 ± 2.1	1.4 ± 0.2	80.4 ± 7.0
9	[Bmim]H_2PO_4	0.9	6.8 ± 0.5	2.5 ± 0.5	90.0 ± 9.0	0.56	5.1 ± 0.9	0.6 ± 0.1	94.0 ± 6.5

[a] Conditions: Pb and Sn working electrodes (0.07 cm^2), Ag/Ag$^+$ reference electrode, and Pt-mesh counter electrode. The full name of the ILs is provided in the experimental section.

mechanism needs to be studied further. We believe that the effect is very complex because the composition influences many properties within the reaction system, such as CO_2 interaction with the electrolyte and the electrode, electrolyte–electrode interactions and mass transfer. All these factors could influence product selectivity.

We also performed the electrochemical reduction of CO_2 in various pure ILs (Supporting Information, Table S2), but the current density in all the ILs was very low. One of the main reasons for this is that the viscosity of the pure ILs is high, which leads to a reduction in the rate of charge transfer on the electrode surface. The reaction was also conducted in $[Bmim]PF_6$/AcN binary electrolytes of different compositions (Supporting Information, Table S3). In $[Bmim]BF_4/H_2O$ binary electrolytes (Supporting Information, Figure S4), the current density is much lower than that in $[Bmim]BF_4$/AcN-H_2O (5 wt%; Supporting Information, Figure S5). We did not perform the reaction in the $[Bmim]PF_6/H_2O$ system because the solubility of H_2O in $[Bmim]PF_6$ was very low. However, the efficiency of electrochemical reduction was still much lower than that in the ternary systems under the optimized conditions. These control experiments demonstrate that the conversion rate of CO_2 is much higher in the ternary system, and H_2O plays a crucial role for achieving very high efficiency. Tables S2 and S3 (Supporting Information) indicate that the Faradaic efficiency of HCOOH in the $[Bmim]PF_6$/AcN binary electrolyte depends strongly on the content of the IL. CO was the main product as the content of IL was very large, which is consistent with observations made for the IL/AcN-H_2O ternary electrolyte systems (Supporting Information, Figure S2).

The effect of applied potential and H_2O content in the ternary mixture is shown in Figure 2. Clearly, adding a suitable amount of H_2O to a $[Bmim]PF_6$ (30 wt%)/AcN mixture can enhance the current density and Faradaic efficiency significantly. Notably, at -2.3 V (vs. Ag/Ag^+) the partial current density reached 37.6 mA cm^{-2} at a Faradaic efficiency of 91.6% in $[Bmim]PF_6$ (30 wt%)/AcN-H_2O (5 wt%) on the Pb electrode. Similarly, the partial current density and Faradaic efficiency on a Sn electrode reached 32.1 mA cm^{-2} and 92.0% in this electrolyte. Other research groups have carried out this reaction by combining various electrodes and electrolytes (Supporting Information, Table S1). As described herein, use of $[Bmim]PF_6$ (30 wt%)/AcN-H_2O (5 wt%) as an electrolyte and Pb or Sn as the electrode clearly achieves a current density much higher than those reported in the literature, including those using noble metal electrodes (Figure 2; Supporting Information, Table S1). Moreover, the electrochemical systems exhibit long-term stability (Figures 2 E,F).

The variation in partial current density of HCOOH on Pb and Sn was studied as a function of applied overpotential (η) in various catholytes (Figures 3 A,B). The Tafel data corresponding to a Pb electrode in the ternary mixture is linear in the 0.06–0.2 V range. Obviously, the overpotential in $[Bmim]PF_6$ (30 wt%)/AcN-H_2O was much lower than that in $[Bmim]PF_6$ (30 wt%)/AcN or $[Bmim]PF_6$. In other words, the presence of H_2O dramatically decreased the overpotential.

Electrochemical impedance spectroscopy (EIS) can provide useful information about the properties of bulk electrolytes and electrode/electrolyte interfaces. To better understand the properties of the electrolyte/Pb interface, a Nyquist plot was obtained by running the experiment at an open circuit potential (Figure 4 A). A simple equivalent circuit R(C(R(W)) was then used to fit the high and medium frequency data (Supporting Information, Figure S6). The charge transfer resistances (R_{ct}) were 4.1, 12.7, and 97.7 kΩ cm^{-2}, when $[Bmim]PF_6$ (30 wt%)/AcN-H_2O (5 wt%), $[Bmim]PF_6$ (30 wt%)/AcN, and $[Bmim]PF_6$ were used as the electrolytes, respectively. This indicates that electron transfer to the electrode surface in $[Bmim]PF_6$ (30 wt%)/AcN-H_2O (5 wt%) is more facile. Double-layer

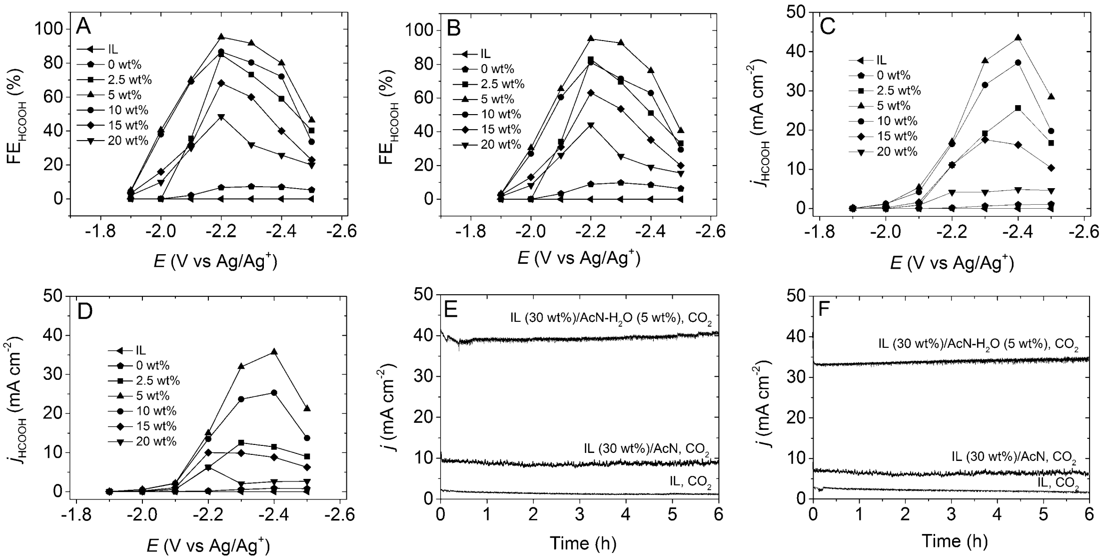

Figure 2. Effect of current density and Faradaic efficiency using $[Bmim]PF_6$ (30 wt%)/AcN-H_2O electrolytes with different H_2O contents. Faradaic efficiency of HCOOH on A) Pb and B) Sn electrodes; partial current density of HCOOH on C) Pb and D) Sn electrodes; the dependence of current density over time on E) Pb and F) Sn electrodes.

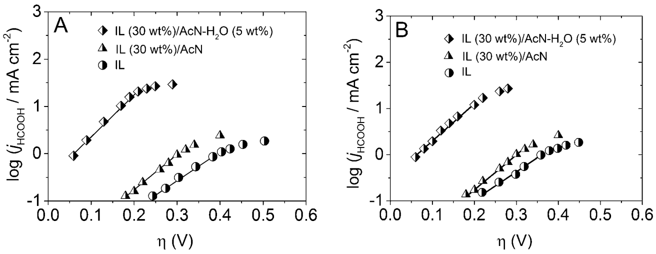

Figure 3. Tafel plots for Pb and Sn electrodes in different CO_2 saturated electrolytes.

capacitance (C_{dl}) calculated from the Nyquist plot in Figure 4A is plotted as a function of H_2O content in Figure 4B. The Pb electrode exhibited a lower C_{dl} in $[Bmim]PF_6$ (30 wt%)/AcN-H_2O (5 wt%), which supports the excellent electrochemical performance of this electrolyte mixture. We also determined the conductivity of the bulk electrolyte (Figure 4B). The conductivity of the electrolyte first increased and then decreased with the increase of H_2O content in $[Bmim]PF_6$ (30 wt%)/AcN, showing a maximum with an H_2O content of 5 wt%. Moreover, addition of H_2O can reduce the onset potential effectively (Supporting Information, Figure S7), delivering the smallest onset potential at 5 wt% H_2O. A decrease in onset potential is favorable when seeking an enhanced current density. Thus, addition of a suitable amount of H_2O can increase the conductivity (Figure 4B), reduce the double-layer capacitance (Figure 4B), and lower the onset potential (Supporting Information, Figure S7). All of these characteristics can enhance the current density, which explains why the addition of a small amount of H_2O is able to enhance current density significantly.

The conductivity of the electrolyte and double-layer capacitance at the electrode/IL interface must be related to the microstructure of the electrolyte. Herein, we studied the microstructure of $[Bmim]PF_6$ (30 wt%)/AcN-H_2O mixtures containing different quantities of H_2O by small-angel X-ray scattering (SAXS), which is a very useful technique for investigating microstructures in solutions. It was reported that ILs form nanoscale aggregates.[19] The scattering curve in Figure 4C moved to a high *q* range with increasing H_2O content ($H_2O < 5$ wt%), illustrating that the size of the IL aggregates decrease according to Bragg's law $d = 2\pi/q$. Moreover, the small size of IL aggregates indicates weaker cation–anion interactions in the electrolyte, which results in higher solubility of CO_2.[20] These two factors are favorable for improving the efficiency of the electrochemical reaction. However, at a higher H_2O content ($H_2O > 5$ wt%), the scattering curve moved slightly to a lower *q* range, suggesting that the size of the aggregates increased with an increase of H_2O content. The SAXS result is consistent with the conductivity data (Figure 4B).

In summary, we have studied the electrochemical reduction of CO_2 into HCOOH on Pb and Sn electrodes in ternary mixtures (IL/AcN/H_2O). It was discovered that both Faradaic efficiency and current density can be easily controlled by tuning the composition of the ternary mixture. In particular, addition of a small amount of H_2O to $[Bmim]PF_6$/AcN or $[Bmim]BF_4$/AcN mixtures can enhance the efficiency of the electrochemical reaction significantly and reduce the overpotential effectively. Using $[Bmim]PF_6$ (30 wt%)/AcN-H_2O (5 wt%) as the electrolyte, current densities as high as 37 and 32 mA cm^{-2} and Faradaic efficiencies as high as 91.6 and 92.0%, were reached on a Pb and Sn electrode, respectively. We believe that the combination of multiple electrolytes and cheap electrodes may provide many opportunities for efficient and economical transformation of CO_2 into valuable chemicals by electrochemical methods.

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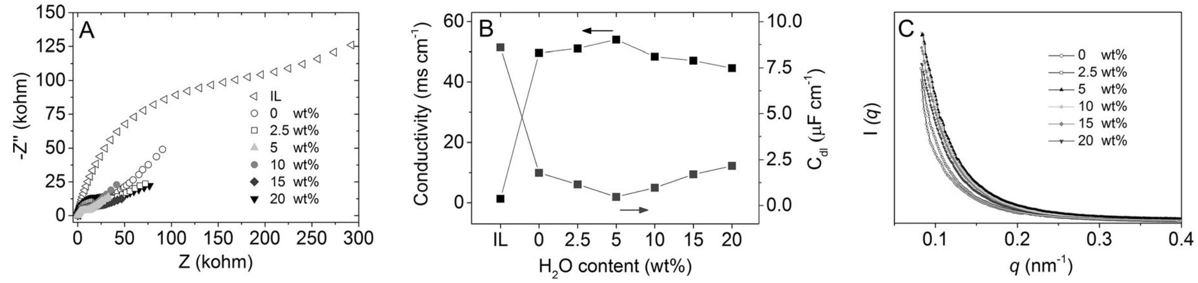

Figure 4. Effect of H_2O content in a $[Bmim]PF_6$(30 wt%)/AcN-H_2O mixture. A) Nyquist plots for a Pb electrode in various electrolytes; B) conductivities and double-layer capacitance of $[Bmim]PF_6$ (30 wt%)/AcN-H_2O mixtures containing different amounts of H_2O (AcN basis); C) SAXS curves of $[Bmim]PF_6$ (30 wt%)/AcN-H_2O with different amounts of H_2O (AcN basis).

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