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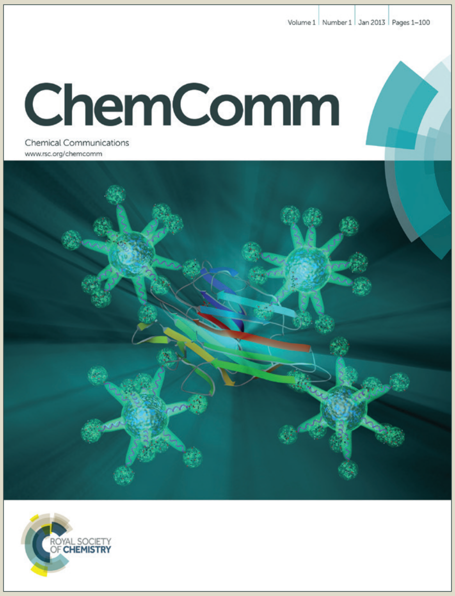

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Ionic liquids enhance the electrochemical CO_2 reduction catalyzed by MoO_2

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Several imidazolium-based ionic liquids significantly enhance the activity of MoO_2 for electrochemical reduction of CO_2. The overpotential of CO_2 reduction is as low as 40 mV. The ionic liquids act as both electrolytes and co-catalysts, which not only leads to lower overpotentials, but also alter the product selectivity.

Recycling of CO_2 to useful products has been considered as an important method towards CO_2 mitigation and utilization.[1] Over the last several decades, intense research efforts have been invested in electrochemical CO_2 reduction.[2-7] While significant progress has been made in the development of new catalysts,[8-14] the number of selective and energy-efficient catalysts remains limited. We earlier reported that MoO_2 was a new and efficient metal oxide-based catalyst for CO_2 reduction in organic solvents such as acetonitrile (MeCN) or dimethylformate (DMF).[15]

Room temperature ionic liquids (RTILs) are regarded as an environmental friendly medium for many chemical processes thanks to their negligible volatility, good solvating ability, and high thermal and chemical stability. Their wide potential windows and intrinsic conductivity,[16, 17] as well the high solubility of CO_2 in them,[18] are all beneficial for electrochemical CO_2 reduction. Recently, some imidazolium-based RTILs are shown to promote electrochemical CO_2 reduction.[11, 19, 20] For example, Masel and co-workers reported that 18 mol% of 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM]BF_4) lowered the overpotential of CO_2 reduction to CO in water on an Ag electrode by about 600 mV.[11] Using Pt as a model substrate, they found that there was a layer of [EMIM] on the electrode, which supressed hydrogen formation and formed a EMIM-CO_2 complex at a mild potential, which could be easily converted to CO.[19] Rosenthal and co-workers found that similar ionic liquids enabled efficient CO_2 reduction to CO on a Bi electrode in MeCN.[13, 14] Inspired by these reports, we tested the possibility of using RTILs to enhance MoO_2-catalyzed electrochemical CO_2 reduction. Here we show that certain ionic liquids indeed improve significantly the CO_2 reduction activity of MoO_2 in MeCN. The formation of CO was promoted and the overpotential of CO_2 reduction was as low as 40 mV.

Fig. 1 shows the linear sweep voltammograms (LSVs) of CO_2 reduction on the MoO_2 (supported on an inert Pb substrate, labelled as MoO_2/Pb) measured in MeCN containing

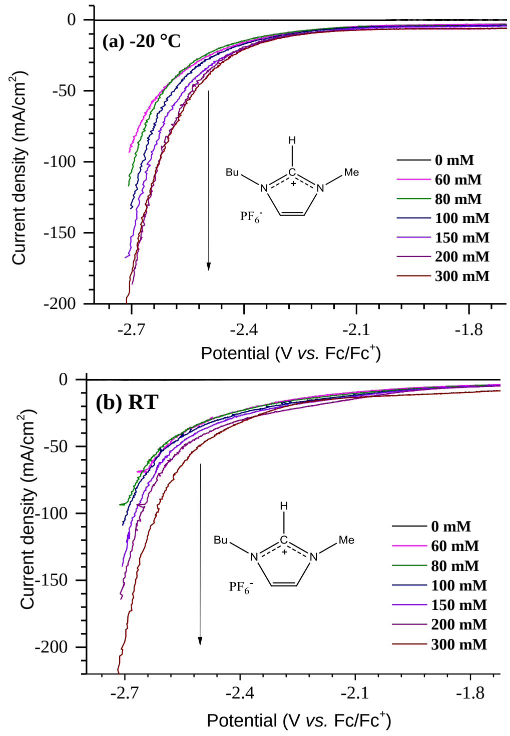

Fig. 1 Linear sweep voltammograms (LSVs) recorded on a MoO_2/Pb electrode in a CO_2-saturated MeCN solution containing varying amounts of [BMIM]PF_6 (a) at -20 °C and (b) at RT; scan rate: 50 mV/s.

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1-butyl-3- methylimidazolium hexafluorophosphate ([BMIM]PF$_6$) as the electrolyte. As described earlier, the lead substrate is preferred over a glassy carbon substrate because it adheres better the MoO$_2$ particles.[15] The addition of [BMIM]PF$_6$ results in similar polarization curves at both temperatures. The polarization curves for CO$_2$ reduction were shifted to more positive potentials when increasing amounts of BMIM PF$_6$ were added into MeCN. At -20 °C, a significant catalytic current for CO$_2$ reduction was observed at about -2.3 V *vs.* the Fc/Fc$^+$ couple (Fig. 1a). At RT and > -2.5 V, the electrocatalytic activity was even higher than at -20 °C (Fig. 2). The catalytic current was observed already at -2.2 V *vs.* Fc/Fc$^+$ (Fig. 1b). At < -2.5 V, the catalytic current densities are similar at both temperatures, probably because the current densities are limited by diffusion of CO$_2$. If CO$_2$ is replaced by N$_2$, the current densities are much lower (Fig. S1, ESI). Without MoO$_2$, the current densities are also much lower (Fig. S2, ESI). As [BMIM]$^+$ itself is reduced only at potentials more negative than -2.8 V *vs.* Fc/Fc$^+$,[14] the catalytic currents observed in Fig. 1 correspond to CO$_2$ reduction. It is interesting to compare the activity of this system to the analogous system using tetrabutylammonium hexafluorophosphate ([TBA]PF$_6$) as the electrolyte (Fig. 2).[15] In the latter system, the catalytic activity is much higher at -20°C than at RT, due to a higher solubility of CO$_2$ at -20°C. In the current system, however, the activity at RT is even better than at -20°C. This is probably because the solubility of CO$_2$ in [BMIM]PF$_6$ at RT is sufficiently high that it does not limit the catalysis compared to at -20°C.[18] Overall, changing the electrolyte from [TBA]PF$_6$ to [BMIM]PF$_6$ significantly improved the catalytic activity at RT (Fig. 2), which is a more practical temperature than -20°C.

Two other imidazolium-based ILs, 1-butyl-3-methylimidazolium chloride and 1-ethyl-3-methylimidazolium hexafluorophosphate ([BMIM]Cl and [EMIM]PF$_6$,) were then used as the electrolytes. Fig. S2 shows the corresponding polarization curves of CO$_2$ reduction on the MoO$_2$/Pb electrode measured in MeCN. The onset potentials of CO$_2$ reduction were observed at about -2.2 to -2.3 V *vs.* Fc/Fc$^+$, similar to when [BMIM]PF$_6$ was used as the electrolyte. The current densities at < -2.45 V *vs.* Fc/Fc$^+$ followed the order of [BMIM]PF$_6$ > [EMIM]PF$_6$ > [BMIM]Cl (Fig. 3), while at more negative potentials, the current density was highest when [EMIM]PF$_6$ was used as the electrolyte. This behaviour should result from the compromise of different factors such as solubility of CO$_2$, mass transport, and co-catalytic activity, which vary independently among different ionic liquids.

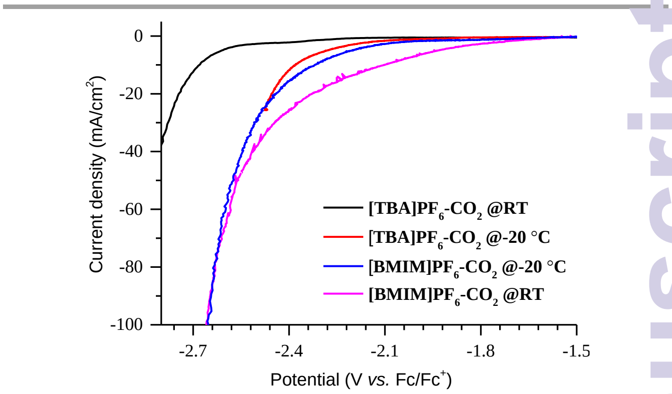


Fig. 2 Linear sweep voltammograms (LSVs) recorded on a MoO$_2$/Pb electrode in a CO$_2$-saturated MeCN solution containing 0.1 M [TBA]PF$_6$ 0.1 M [BMIM]PF$_6$ at two different temperatures; scan rate: 50 mV/s.

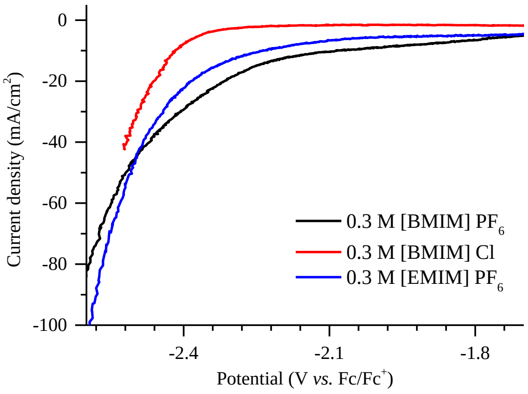


Fig. 3 Linear sweep voltammograms (LSVs) recorded at RT on a MoO$_2$/P electrode in a CO$_2$-saturated MeCN solution containing 0.3 M of differe ionic liquids; scan rate: 50 mV/s.

The results suggest that not only the cations, but also the anions play a role. For the conversion of CO$_2$ to CO in MeCN, the value $E°_{CO2/CO}$ can be calculated by equation (1): [12]

$$E°_{CO2/CO} = 0.105 - \frac{RT \times \ln(10)}{F} pKa(\mathrm{HA, MeCN})\ \mathrm{V} \quad (vs.\ \mathrm{SCE}) \quad (1)$$

The *pKa* values of 1,3-dialkylimidazolium cations are about 32 in MeCN.[21] Therefore, assuming that the proton source is the IL, $E°_{CO2/CO}$ is -1.78 V *vs.* SCE, equivalent to -2.18 V *vs.* Fc/Fc$^+$.[22, 23] The onset potential of CO$_2$ reduction in the presence of [BMIM]PF$_6$ is around -2.22 V *vs.* Fc/Fc$^+$ (Fig. 1b), which indicates that CO$_2$ reduction occurs at an overpotential as low as 40 mV. The onset overpotential is among the lowest for CO$_2$ reduction under similar conditions. As a reference, Bi electrode, a recently reported highly active catalyst for CO$_2$ reduction in MeCN, has an overpotential of more than 100 mV using [EMIM]PF$_6$ as the electrolyte and co-catalyst. [13, 14]

Fig. S3 shows the time-dependent current response of potentiostatic electrolysis measurements of CO$_2$ reduction on MoO$_2$/Pb electrode in 0.3 M [BMIM]PF$_6$/MeCN solution at RT. At 2.30 V *vs.* Fc/Fc$^+$, the current density gradually decreased from more than -10 mA cm^{-2} to about -7 mA cm^{-2} in 20 min; the initial current density might contain contributions from side processes such as the reduction of PbO in the substrate and other unidentified reactions. However, at -2.45 V *vs.* Fc/Fc$^+$, the current density remained constant at about -20 mA cm^{-2} during this period, suggesting that the current densities from the side processes were negligible compared to that from CO_2 reduction at this potential. The stable current densities at both potentials are comparable to those of CO_2 reduction on a Bi electrode in combination with a similar ionic liquid.[13, 14]

The products of CO_2 reduction were determined after long-term potentiostatic electrolysis experiments. In all cases, CO was the only gaseous product. No significant H_2 formation was detected. Formate and oxalate were detected in the liquid phase. These products (CO, formate and oxalate) were not formed when the electrolysis was carried out in a N_2-saturated condition, confirming that they are produced from electrocatalytic CO_2 reduction.

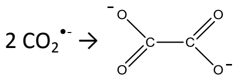
Table 1. Potential-dependent Faradaic efficiency of the formation of CO, formate and oxalate from electrocatalytic CO_2 reduction; conditions: MoO_2/Pb electrode; 0.3 M [BMIM]PF6 as electrolyte. Data were obtained from -20 °C and at room temperature.

Entry	Temp. (°C)	Potential (V *vs.* Fc/Fc$^+$)	Faradaic efficiency (%)				
			H_2	CO	$C_2O_4^{2-}$	$HCOO^-$	Total
1	-20	-2.30	.	27.8	0.9	59.3	88.0
2	-20	-2.45	.	39.8	.	19.4	59.2
3	-20	-2.60	.	64.8	.	12.6	77.4
4	21	-2.30	.	21.8	8.2	60.9	90.9
5	21	-2.45	.	41.6	6.2	38.2	86.0
6	21	-2.60	.	63.3	4.1	19.6	87.0

Table 1 presents the product distribution of CO_2 reduction and the corresponding Faradaic efficiency as a function of potential. The selectivity and Faradaic efficiency are similar at RT and -20 ^{o}C. This result is in contrast to analogous CO_2 reduction using 0.1 M $TBAPF_6$ as the electrolyte,[15] where the selectivity depended on the temperature. In the current system, the Faradaic efficiency of CO is higher at more negative potentials and reached 65% at -2.6 V *vs.* Fc/Fc$^+$. On the contrary, the Faradaic efficiency of formate formation was decreased from about 60% at -2.30 V to below 20% at -2.60 V. The total Faradaic efficiency for CO and formate exceeded 80% in all cases. Oxalate was formed only in a low percentage at all potentials. Fig. S4 shows the Faradaic efficiency of carbon monoxide, formate and oxalate for the CO_2 reduction on the MoO_2/Pb electrode using [BMIM]Cl and [EMIM]PF_6 as electrolytes. A similar trend to that in Table 1 was observed.

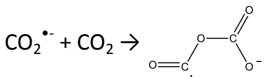
The mechanism of CO_2 reduction in organic solvents can be described as follows:[24, 25]

$$CO_2 + e^- \rightarrow CO_2^{\bullet -} \qquad (2)$$



(3)

$$CO_2^{\bullet -} + H^+ + e^- \rightarrow CO + OH^- \qquad (4)$$



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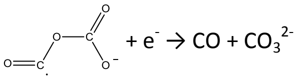

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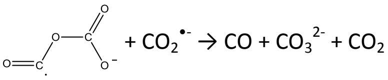

(7)

$$CO_2^{\bullet -} + H_2O \rightarrow HCO_2^{\bullet} + OH^- \qquad (8)$$

$$HCO_2^{\bullet} + e^- \rightarrow HCO_2^- \qquad (9)$$

$$HCO_2^{\bullet} + CO_2^{\bullet -} \rightarrow HCO_2^- + CO_2 \qquad (10)$$

The first step is the reduction of CO^2 to give $CO_2^{\bullet -}$ radical. Dimerization of $CO_2^{\bullet -}$ gives oxalate. CO might be produced through two different pathways: one involves the protonation of $CO_2^{\bullet -}$ by trace water or a protic solvent (eqn (4)), while the other involves the reaction of $CO_2^{\bullet -}$ with CO_2 to give CO and carbonate (eqn (7)). Formate, on the other hand, can only be produced with a proton source (eqn (8)-(10)).

For CO_2 reduction on MoO_2 using [TBA]PF_6 as the supporting electrolyte in dry MeCN, the predominant product was oxalate.[15] By replacing [TBA]PF_6 with [BMIM]PF_6, the predominant product is changed to CO. A similar result was obtained on [EMIM]-promoted CO_2 reduction on Pb in MeCN, where the replacement of tetraethylammonium perchlorate ([TEA]ClO_4) by [EMIM] bis(trifluoromethylsulfonyl)imide shifted the dominant product from oxalate to CO as well.[20] It was proposed that $CO_2^{\bullet -}$ was stabilized by the absorbed layer of imidazolium cation at the electrode surface,[19, 20] which prevented the dimerization of two $CO_2^{\bullet -}$ to form oxalate. A similar mechanism is proposed here. The stabilization of $CO_2^{\bullet -}$ also explains the decrease of the overpotentials of the current system. Because tetraalkylammonium salts were required for electrochemical and photochemical reduction of CO_2 on certain electrodes, it was proposed that they could be reduced to neutral radicals, which in terms transferred electrons to CO_2.[26] A recent study indicates that the reduction of

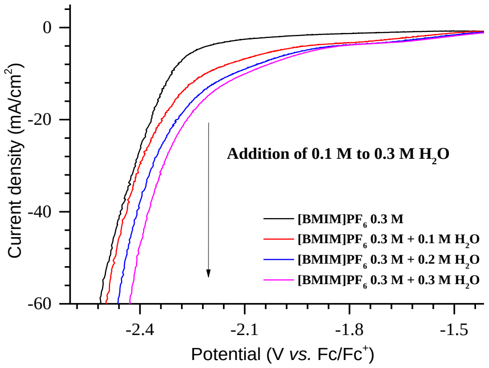

Fig. 4 Influence of water concentration on the polarization curves of MoO_2/Pb in CO_2-saturated MeCN at RT. Electrolyte: 0.3 M [BMIM]PF_6; Scan rate: 50 mV/s.

tetraalkylammonium salts in those systems is not viable, and these salts likely serve to prevent surface passivation of electrodes.[27] The fact that [TBA]PF_6 can be replaced by ILs in CO_2 reduction on MoO_2 further supports the non-catalytic role of tetraalkylammonium salts.

The influence of water in the electrochemical reduction of CO_2 in this system was probed by addition of a known concentration of water into the electrolyte solution at RT. Fig. 4 shows that the polarization curves of CO_2 reduction were shifted to more positive potentials when an increasing amount of water was added. Table 2 shows the product distribution of CO_2 reduction under these conditions at -2.45 V *vs.* Fc/Fc^+. At 0.1 M water concentration, the Faradaic yield of CO was increased from 40% to 60%, at the expense of formate. However, a further increase in water concentration then reduced the Faradaic yields of both CO and formate due to competitive H_2 formation.

Table 2. Faradaic efficiency and the product distribution of CO_2 reduction as a function of water concentration. Potentiostatic electrolysis was measured on a MoO_2/Pb electrode at -2.45 V *vs.* Fc/Fc^+ at RT in 0.3M [BMIM]PF_6/MeCN.

Concentration of water (M)	Potential (V *vs.* Fc/Fc^+)	Faradaic efficiency (%)				
		H_2	CO	$C_2O_4^{2-}$	$HCOO^-$	Total
0.1	-2.45	12.4	60.8	5.3	17.8	96.3
0.2	-2.45	25.1	51.7	5.5	9.8	92.1
0.3	-2.45	28.9	51.4	4.3	6.2	90.8

In conclusion, the electrochemical reduction of CO_2 on MoO_2 in MeCN can be significantly enhanced using several imidazolium-based ionic liquids, with the best results obtained using [BMIM]PF_6. High activity can be obtained at room temperature instead of -20 °C, which was previously required using [TBA]PF_6 as the electrolyte. The overpotential for CO_2 reduction is as low as 40 mV. Replacement of [TBA]PF_6 by ILs promoted the formation of CO and suppressed the formation of oxalate. The improvement in catalytic activity and the change of product selectivity suggest that the ILs have a co-catalyst role.

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