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Ionic liquids enhance the electrochemical CO2 reduction catalyzed by MoO2

Yeonji Oh and Xile Hu*

Several imidazolium-based ionic liquids significantly enhance the activity of MoO2 for electrochemical reduction of CO2. The overpotential of CO2 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 CO2 to useful products has been considered as an important method towards CO2 mitigation and utilization.1 Over the last several decades, intense research efforts have been invested in electrochemical CO2 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 MoO2 was a new and efficient metal oxide-based catalyst for CO2 reduction in organic solvents such as acetonitrile (MeCN) or dimethylformamide (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 as the high solubility of CO2 in them,18 are all beneficial for electrochemical CO2 reduction. Recently, some imidazolium-based RTILs are shown to promote electrochemical CO2 reduction.11, 19, 20 For example, Masel and co-workers reported that 18 mol% of 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM]BF4) lowered the overpotential of CO2 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 suppressed hydrogen formation and formed a EMIM-CO2 complex at a mild potential, which could be easily converted to CO.19 Rosenthal and co-workers found that similar ionic liquids enabled efficient CO2 reduction to CO on a Bi electrode in MeCN.13, 14 Inspired by these reports, we tested the possibility of using RTILs to enhance MoO2-catalyzed electrochemical CO2 reduction. Here we show that certain ionic liquids indeed improve significantly the CO2 reduction activity of MoO2 in MeCN. The formation of CO was promoted and the overpotential of CO2 reduction was as low as 40 mV.

Fig. 1 shows the linear sweep voltammograms (LSVs) of CO2 reduction on the MoO2 (supported on an inert Pb substrate labelled as MoO2/Pb) measured in MeCN containing EMIM-CF3SO3 at 0, 60, 80, 100, 150, 200, and 300 mM. The overpotential of CO2 reduction was as low as 40 mV at 200 mM EMIM-CF3SO3. The linear sweep voltammograms of CO2 reduction on a MoO2/Pb electrode in MeCN containing EMIM-CF3SO3 at 0, 60, 80, 100, 150, 200, and 300 mM. The overpotential of CO2 reduction was as low as 40 mV at 200 mM EMIM-CF3SO3.

Fig. 1 Linear sweep voltammograms (LSVs) recorded on a MoO2/Pb electrode in a CO2-saturated MeCN solution containing varying amounts of [BMIM]PF6 (a) at -20 °C and (b) at RT; scan rate: 50 mV/s.
1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF₆) as the electrolyte. As described earlier, the lead substrate is preferred over a glassy carbon substrate because it adheres better to the MoO₂ particles. The addition of [BMIM]PF₆ results in similar polarization curves at both temperatures. The polarization curves for CO₂ reduction were shifted to more positive potentials when increasing amounts of BMIM PF₆ were added into MeCN. At -20 °C, a significant catalytic current for CO₂ 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 CO₂. If CO₂ is replaced by N₂, the current densities are much lower (Fig. S1, ESI). Without MoO₂, 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', the catalytic currents observed in Fig. 1 correspond to CO₂ reduction. It is interesting to compare the activity of this system to the analogous system using tetraethylammonium hexafluorophosphate ([TBA]PF₆) as the electrolyte (Fig. 2). In the latter system, the catalytic activity is much higher at -20°C than at RT, due to a higher solubility of CO₂ 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 CO₂ in [BMIM]PF₆ at RT is sufficiently high that it does not limit the catalysis compared to at -20°C. Overall, changing the electrolyte from [TBA]PF₆ to [BMIM]PF₆ 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 ([EMIM]PF₆) were then used as the electrolytes. Fig. S2 shows the corresponding polarization curves of CO₂ reduction on the MoO₂/Pb electrode measured in MeCN. The onset potentials of CO₂ reduction were observed at about -2.2 to -2.3 V vs. Fc/Fc', similar to when [BMIM]PF₆ was used as the electrolyte. The current densities at -2.45 V vs. Fc/Fc' followed the order of [BMIM]PF₆ > [EMIM]PF₆ > [BMIM]Cl (Fig. 3), while at more negative potentials, the current density was highest when [EMIM]PF₆ was used as the electrolyte. This behaviour should result from the compromise of different factors such as solubility of CO₂, mass transport, and cocatalytic activity, which vary independently among different ionic liquids.

The results suggest that not only the cations, but also the anions play a role. For the conversion of CO₂ to CO in MeCN, the value of $E'_{CO2/CO}$ can be calculated by equation (1): $E'_{CO2/CO} = 0.105 - \frac{RT \times \ln(10) k_B}{F} p_{CO2} (HA, MeCN) V$ (vs. SCE) (1).

The $pK_a$ values of 1,3-dialkylimidazolium cations are about 32 in MeCN. 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'. The onset potential of CO₂ reduction in the presence of [BMIM]PF₆ is around -2.22 V vs. Fc/Fc' (Fig. 1b), which indicates that CO₂ reduction occurs at an overpotential as low as 40 mV. The onset overpotential is among the lowest for CO₂ reduction under similar conditions. As a reference, Bi electrode, a recently reported highly active catalyst for CO₂ reduction in MeCN, has an overpotential of more than 100 mV using [EMIM]PF₆ as the electrolyte and catalyst. Fig. S3 shows the time-dependent current response of potentiostatic electrolysis measurements of CO₂ reduction on the MoO₂/Pb electrode in 0.3 M [BMIM]PF₆/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>
<thead>
<tr>
<th>Entry</th>
<th>Temp. (°C)</th>
<th>Potential (V vs. Fc/Fc')</th>
<th>Faradaic efficiency (%)</th>
<th>H(_2)</th>
<th>CO</th>
<th>C(_2)O (\rightarrow) CO(_2)</th>
<th>C(_2)O</th>
<th>HCOO</th>
<th>Total</th>
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<td>21.8</td>
<td>8.2</td>
<td>60.9</td>
<td>90.9</td>
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<td>-2.45</td>
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<td>4.1</td>
<td>19.6</td>
<td>87.0</td>
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</table>

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 °C. This result is in contrast to analogous CO\(_2\) reduction using 0.1 M TBA\(\text{PF}_6\) as the electrolyte,\(^{15}\) where the selectivity depended on the temperature. In the current system, the Faradaic efficiency of CO\(_2\) 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:\(^{24,25}\)

\[
\text{CO}_2 + e^- \rightarrow \text{CO}_2^* \quad (2)
\]

\[
2 \text{CO}_2^* \rightarrow \text{O} = \text{C} - \text{O} \quad (3)
\]

\[
\text{CO}_2^* + \text{H}^+ + e^- \rightarrow \text{CO} + \text{OH}^- \quad (4)
\]

The first step is the reduction of CO\(^2\) to give CO\(_2^*\) radicals. Dimerization of CO\(_2^*\) gives oxalate. CO might be produced through two different pathways: one involves the protonation of CO\(_2^*\) by trace water or a protic solvent (eqn (4)), while the other involves the reaction of CO\(_2^*\) with CO 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\(_2/Pb\) using [TBA]PF\(_6\) as the supporting electrolyte in dry MeCN, the predominant product was oxalate.\(^{26}\) For 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\(_2^*\) was stabilized by the absorbed layer of imidazolium cation at the electrode surface,\(^{19,20}\) which prevented the dimerization of two CO\(_2^*\) to form oxalate. A similar mechanism is proposed here. The stabilization of CO\(_2^*\) also explains the decrease of the overpotentials of the current system. Because tetraethylammonium 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 turn transmuted electrons to CO\(_2\).\(^{26}\) A recent study indicates that the reduction of
tetraalkylammonium salts in those systems is not viable, and these salts likely serve to prevent surface passivation of electrodes. 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.

<table>
<thead>
<tr>
<th>Concentration of water (M)</th>
<th>Potential (V vs. Fc/Fc$^+$)</th>
<th>H$_2$</th>
<th>CO</th>
<th>C$_2$O$_4^{2-}$</th>
<th>HCOO$^-$</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>-2.45</td>
<td>12.4</td>
<td>60.8</td>
<td>5.3</td>
<td>17.8</td>
<td>96.3</td>
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<tr>
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<td>28.9</td>
<td>51.4</td>
<td>4.3</td>
<td>6.2</td>
<td>90.8</td>
</tr>
</tbody>
</table>

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 $^\circ$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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**Notes and references**


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