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## Acid-Base Interaction Enhancing Oxygen Tolerance in Electrocatalytic Carbon Dioxide Reduction

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### Abstract

Catalytic electrodes with the capability to directly convert atmospheric CO<sub>2</sub> into value-added products are of potential environmental and economic benefit, but entail an effective CO<sub>2</sub> selection strategy to impede the competing O<sub>2</sub> reduction reaction. In this work, we have developed a new generation of hybrid electrodes with improved O<sub>2</sub> tolerance and unprecedented capability of CO<sub>2</sub> conversion to liquid products in the presence of O<sub>2</sub>. We introduce aniline molecules into the pore structure of a polymer of intrinsic microporosity to expand its gas separation functionality beyond pure physical sieving. The chemical interaction between the acidic CO<sub>2</sub> molecule and the basic amino group of aniline renders enhanced CO<sub>2</sub> separation from O<sub>2</sub>. Loaded with a cobalt phthalocyanine-based cathode catalyst, our hybrid electrode achieves a CO Faradaic efficiency of 71% with 10% O<sub>2</sub> in the CO<sub>2</sub> feed gas. The electrode can still perform CO production at an O<sub>2</sub>/CO<sub>2</sub> ratio as high as 9:1. Switching to a Sn-based catalyst, we for the first time realize O<sub>2</sub>-tolerant CO<sub>2</sub> electroreduction to liquid products, generating formate with nearly 100% selectivity and a current density of 56.7 mA/cm<sup>2</sup> in the presence of 5% O<sub>2</sub>.

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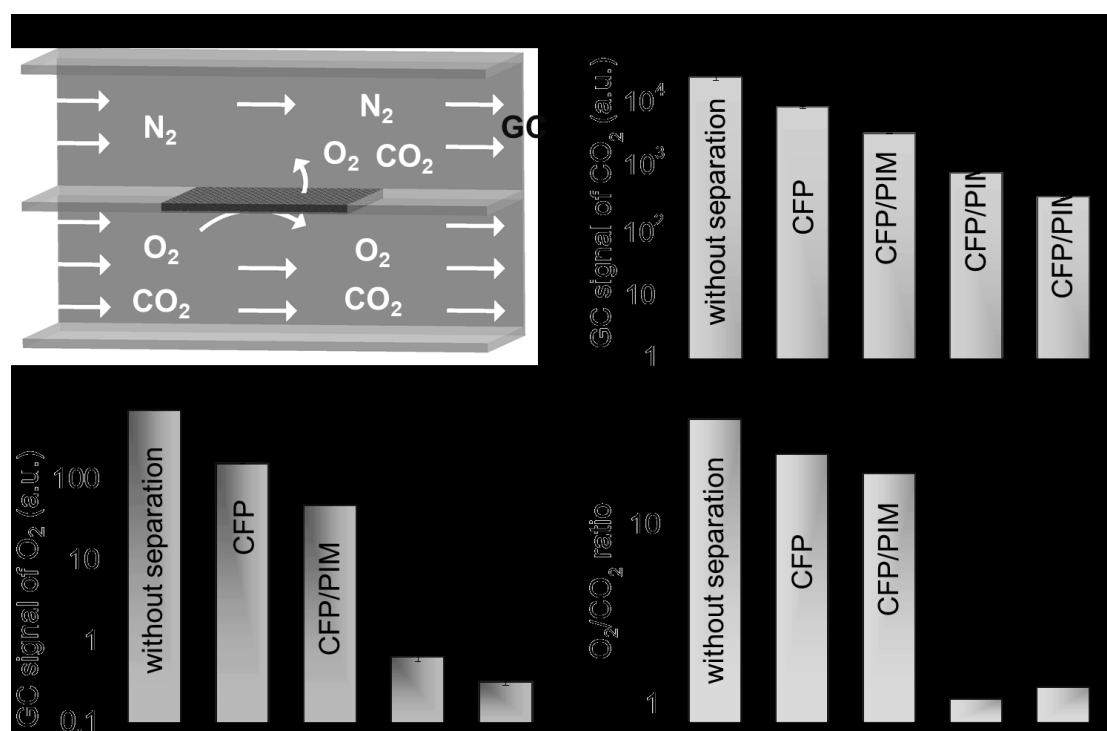
Electrochemical CO<sub>2</sub> reduction driven by renewable energy sources is an attractive strategy for converting CO<sub>2</sub> to value-added carbon-based products.<sup>1-7</sup> If achieved on a large scale, it could help alleviate the global warming and ocean acidification issues.<sup>8-9</sup> For this process to be more commercially relevant, the CO<sub>2</sub> reactant should come from practical sources such as combustion exhaust and ambient air,<sup>10-11</sup> both of which contain a substantial amount of O<sub>2</sub>. However, in a realistic electrolytic cell without mass transport limitation, the CO<sub>2</sub> reduction reactions can be completely inhibited by as little as 5% O<sub>2</sub> in CO<sub>2</sub> because of the considerable difference in their standard reduction electrode potentials.<sup>10, 12-15</sup> It is therefore challenging yet potentially highly rewarding to develop a catalytic electrode that can directly valorize O<sub>2</sub>-containing CO<sub>2</sub> gases without requiring additional energy input for reactant purification.

In our prior work, we designed the first O<sub>2</sub>-tolerant catalytic electrode for CO<sub>2</sub> reduction. Our design was to integrate a CO<sub>2</sub> reduction electrocatalyst with a polymer of intrinsic microporosity (PIM) layer that can selectively permeate CO<sub>2</sub> from its O<sub>2</sub> mixture.<sup>10</sup> This electrode was able to generate CO with a Faradaic efficiency (FE) of 75.9% from CO<sub>2</sub> containing 5% O<sub>2</sub>. Despite this progress, it is still necessary to further improve O<sub>2</sub> tolerance of the electrode and expand the scope of products. Considering that PIM separates CO<sub>2</sub> from O<sub>2</sub> via a physical process through its size-selective pores,<sup>16-17</sup> we believe there is opportunity to enhance the separation process by introducing chemical interactions.

Here, we report a second generation of O<sub>2</sub>-tolerant catalytic electrodes for CO<sub>2</sub> reduction, which are developed from their predecessors by introducing guest aniline molecules into the PIM structure and by changing the electrocatalyst. Benefited from the chemical interaction between acidic CO<sub>2</sub> and the basic amino group of aniline, the PIM/aniline hybrid membrane demonstrates improved CO<sub>2</sub> vs O<sub>2</sub> selectivity compared to pure PIM. Deployed in an electrolytic flow cell, our electrode comprising such a hybrid gas selection layer and a catalyst layer of cobalt phthalocyanine (CoPc) molecules anchored on carbon nanotubes (CNTs) achieves a FE<sub>CO</sub> of 71% in the presence of 10% O<sub>2</sub> in CO<sub>2</sub>. At a high O<sub>2</sub>/CO<sub>2</sub> ratio of 9:1, the electrode can still have net CO<sub>2</sub> conversion, whereas the control electrode without aniline completely loses its function. Switching the catalyst to Sn particles allows us to expand our

products beyond CO and realize the first selective reduction of CO<sub>2</sub> to formate in the presence of 5% O<sub>2</sub>.

We first used a gas separation experiment (see Supporting Information for details), where a CO<sub>2</sub>/O<sub>2</sub> mixture gas with a fixed volume ratio of 1:39 flows through the channel on one side of the gas diffusion electrode (GDE) and a N<sub>2</sub> carrier gas flows on the other side for gas sampling (**Figure 1a**), to study the amounts of CO<sub>2</sub> and O<sub>2</sub> penetrating the GDE. The GDE was a carbon fiber paper (CFP) or a CFP with a gas selection layer drop-casted on the side facing the CO<sub>2</sub>/O<sub>2</sub> mixture gas channel. As can be seen from the gas chromatography (GC) peak areas, the CFP alone can reject both CO<sub>2</sub> and O<sub>2</sub> to some extent (**Figure 1b** and **c**). CFP coated with a layer of PIM can more effectively limit CO<sub>2</sub> and O<sub>2</sub> penetration and decrease the O<sub>2</sub>/CO<sub>2</sub> ratio compared to the CFP-only case. When the PIM layer is infiltrated with aniline or toluene, gas (especially O<sub>2</sub>) penetration is further suppressed. In the aniline case, we observed the smallest O<sub>2</sub>/CO<sub>2</sub> ratio among all the electrode configurations (**Figure 1d**), revealing its highest CO<sub>2</sub>/O<sub>2</sub> selectivity in spite of the lower CO<sub>2</sub> permeability caused by small molecule incorporation in the PIM structure (**Figure 1b**).

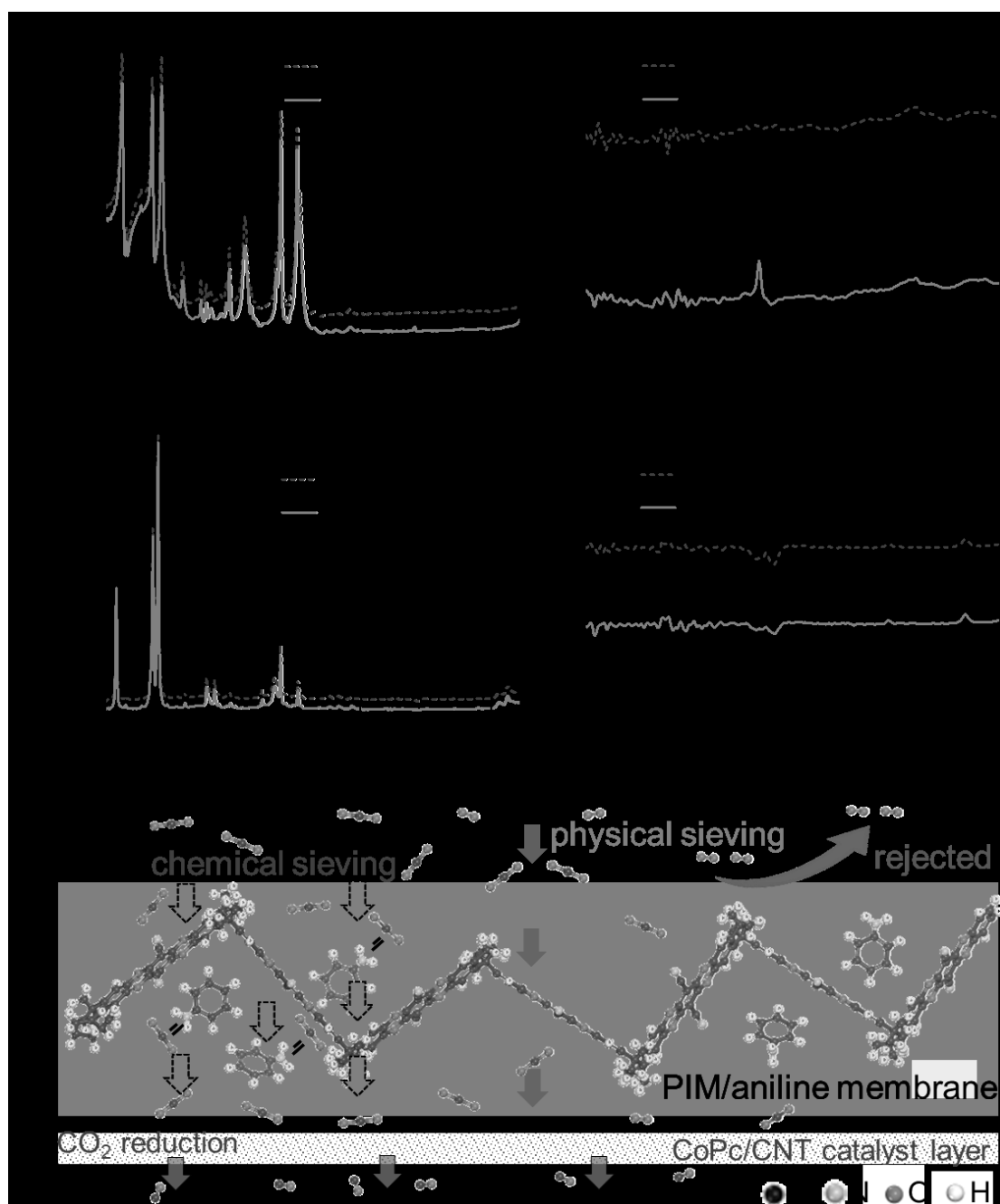


**Figure 1.** (a) Schematic diagram of gas separation setup for measuring the selectivity of membrane for CO<sub>2</sub> separation from O<sub>2</sub>. (b) CO<sub>2</sub> and (c) O<sub>2</sub> signals detected by GC for the

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effluent of the N<sub>2</sub> channel with different GDEs. Error bars represent standard deviations from multiple GC samplings. (d) O<sub>2</sub>/CO<sub>2</sub> volume ratios in the effluent of the N<sub>2</sub> channel with different GDEs.

We conducted infrared (IR) spectroscopy measurements to understand the enhancing effect of aniline on PIM for CO<sub>2</sub> separation from O<sub>2</sub>. The IR spectra of aniline and toluene before and after 1 h of CO<sub>2</sub> bubbling into these two liquids are plotted in **Figures 2a-d**. Interestingly, the asymmetrical stretching band of CO<sub>2</sub> is clearly observed at approximately 2335 cm<sup>-1</sup> for the CO<sub>2</sub>-treated aniline sample,<sup>18-19</sup> while no such peak is found in the case of toluene. The observation of the CO<sub>2</sub> peak and its decrease in wavenumber relative to a free CO<sub>2</sub> molecule (2349 cm<sup>-1</sup>)<sup>20</sup> indicates that CO<sub>2</sub> is likely adsorbed by aniline via the chemical interaction between the acidic CO<sub>2</sub> and the basic amino group of aniline.<sup>21-22</sup> In fact, amino groups are often incorporated into metal-organic framework structures to enhance their CO<sub>2</sub> adsorption capacity.<sup>23-24</sup> **Figure 2e** depicts the roles played by aniline in the improved CO<sub>2</sub> vs O<sub>2</sub> separation of the PIM/aniline material: On the one hand, the aniline molecules residing in the pore structure of PIM create a physical barrier, which enhances the rejection of the bigger O<sub>2</sub> (kinetic diameter 0.35 nm)<sup>25</sup> molecules to a greater extent compared to the smaller CO<sub>2</sub> (0.33 nm)<sup>26</sup> molecules. This would result in a lower gas permeability but a higher CO<sub>2</sub>/O<sub>2</sub> selectivity. On the other hand, the amino group of aniline can selectively enhance CO<sub>2</sub> transport via acid-base interactions. In the absence of amino groups, the PIM/toluene membrane separates CO<sub>2</sub> from O<sub>2</sub> solely through physical sieving. Therefore, the CO<sub>2</sub>/O<sub>2</sub> selectivity of PIM/toluene is higher than pure PIM but lower than PIM/aniline.

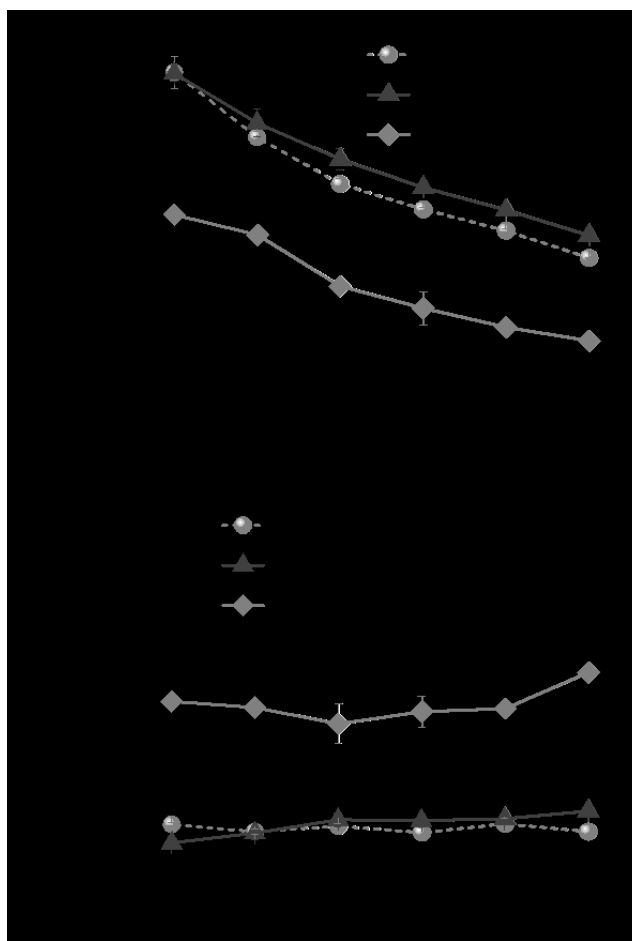


**Figure 2.** IR spectra of (a, b) aniline and (c, d) toluene before and after interacting with CO<sub>2</sub>. (e) Schematic diagram of enhanced CO<sub>2</sub>/O<sub>2</sub> separation and O<sub>2</sub>-tolerant catalytic CO<sub>2</sub> reduction on a hybrid electrode with PIM/aniline.

Based on the gas separation results, we anticipate the PIM/aniline-containing GDE would improve electrocatalytic CO<sub>2</sub> reduction in the presence of O<sub>2</sub>, although the separation performance may not be directly translated into electrochemical performance because of their different conditions. To perform electrochemical CO<sub>2</sub> reduction reaction studies, we used CoPc

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molecules supported on CNTs (CoPc/CNT) as the catalyst,<sup>3, 10, 27-28</sup> which was coated onto the other side of the CFP supporting PIM/aniline (see Supporting Information). A gas-diffusion electrochemical cell as reported in our previous work was used.<sup>10, 28</sup> The cell voltage was optimized to be 3.4 V for achieving highest CO<sub>2</sub> reduction selectivity (**Figure S1**). **Figure 3** and **Figure S2** show the FE<sub>CO</sub> and total current density ( $j_{\text{total}}$ ) for the reduction reactions of CO<sub>2</sub>/O<sub>2</sub> mixtures containing different percentages of O<sub>2</sub>. The PIM/aniline electrode operating with 10% O<sub>2</sub> exhibits a FE<sub>CO</sub> of 71% and a  $j_{\text{total}}$  of 30.6 mA/cm<sup>2</sup>, outperforming the corresponding PIM electrode which affords a FE<sub>CO</sub> of 63% under the same conditions. The improved FE<sub>CO</sub> is consistent with the improved CO<sub>2</sub> vs O<sub>2</sub> selectivity observed in the gas separation experiments (**Figure 1d**). The reasonably high current density indicates that mass transport of CO<sub>2</sub>, although suppressed by the PIM/aniline layer (**Figure 1b**), is not compromising the reaction rate. In contrast, the PIM/toluene electrode, which lacks chemical interaction between toluene and CO<sub>2</sub>, shows a FE<sub>CO</sub> of 33% with a  $j_{\text{total}}$  of 29.3 mA/cm<sup>2</sup> at the same conditions, lower in selectivity and activity for CO production than that of the PIM electrode. The poor CO<sub>2</sub> reduction efficiency can be attributed to the low gas permeability of the PIM/toluene membrane, which hampers CO<sub>2</sub> delivery to the catalytic sites, in line with the gas separation results (**Figure 1b** and **c**). Consistently, H<sub>2</sub> evolution becomes more dominant (**Figure 3b**). For all these three catalytic electrodes, FE<sub>CO</sub> gradually decreases when the O<sub>2</sub> content of the feed gas increases, and the PIM/aniline electrode always gives the highest FE<sub>CO</sub> among the three at any fixed O<sub>2</sub> concentration (**Figure 3a**). Further control experiments with PIM/benzene (**Figures S3** and **S4**) and PIM/phenol (**Figures S5** and **S6**) electrodes give similar results to the PIM/toluene electrode, confirming the critical role of the amino group in the aniline molecular structure in enhancing CO<sub>2</sub> selection via acid-base interaction.

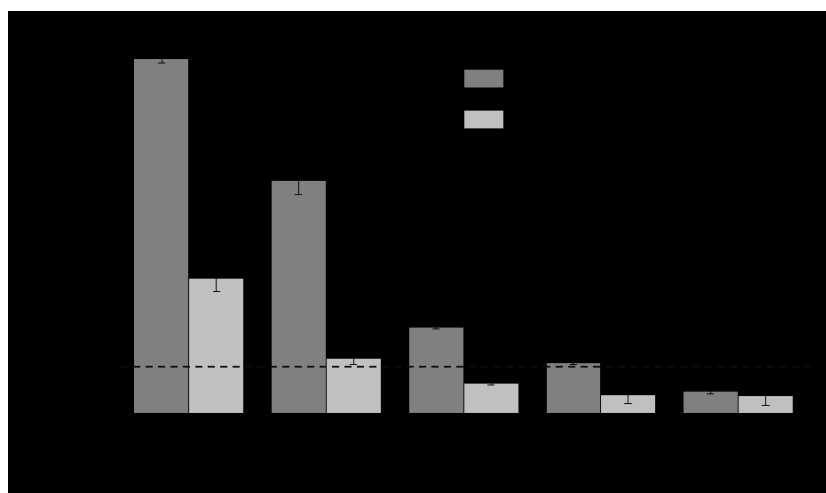


**Figure 3.** (a)  $FE_{CO}$  and (b)  $FE_{H_2}$  for PIM, PIM/aniline and PIM/toluene cathodes operating with  $CO_2/O_2$  feed gas containing different  $O_2$  percentages. Electrolyte: 0.5 M aqueous  $KHCO_3$ ; Cathode catalyst: CoPc/CNT; Anode catalyst:  $CoO_x$ /CNT; Cell voltage: 3.4 V. Error bars represent standard deviations from multiple measurements.

Incorporation of aniline in the PIM layer extends the range of  $O_2/CO_2$  feed ratio under which the catalytic electrode can effectively convert  $CO_2$  to CO. When operating in a gas mixture containing 40%  $O_2$ , 10%  $CO_2$  and 50%  $N_2$  ( $N_2$  is blended in because it is a major component of air and typical flue gases<sup>29</sup>), the PIM electrode cannot effectively catalyze  $CO_2$  reduction, with its measured CO production rate at the same level as the instrument noise in this case (**Figure 4**), whereas the PIM/aniline electrode can still produce CO at a rate that is five times higher (**Figure 4**). When the  $O_2/CO_2$  ratio is further increased to 9:1, the PIM/aniline electrode can still perform  $CO_2$  reduction at a rate significantly higher than the noise level (**Figure 4**). This represents another small step toward the ultimate goal of direct  $CO_2$  valorization from the

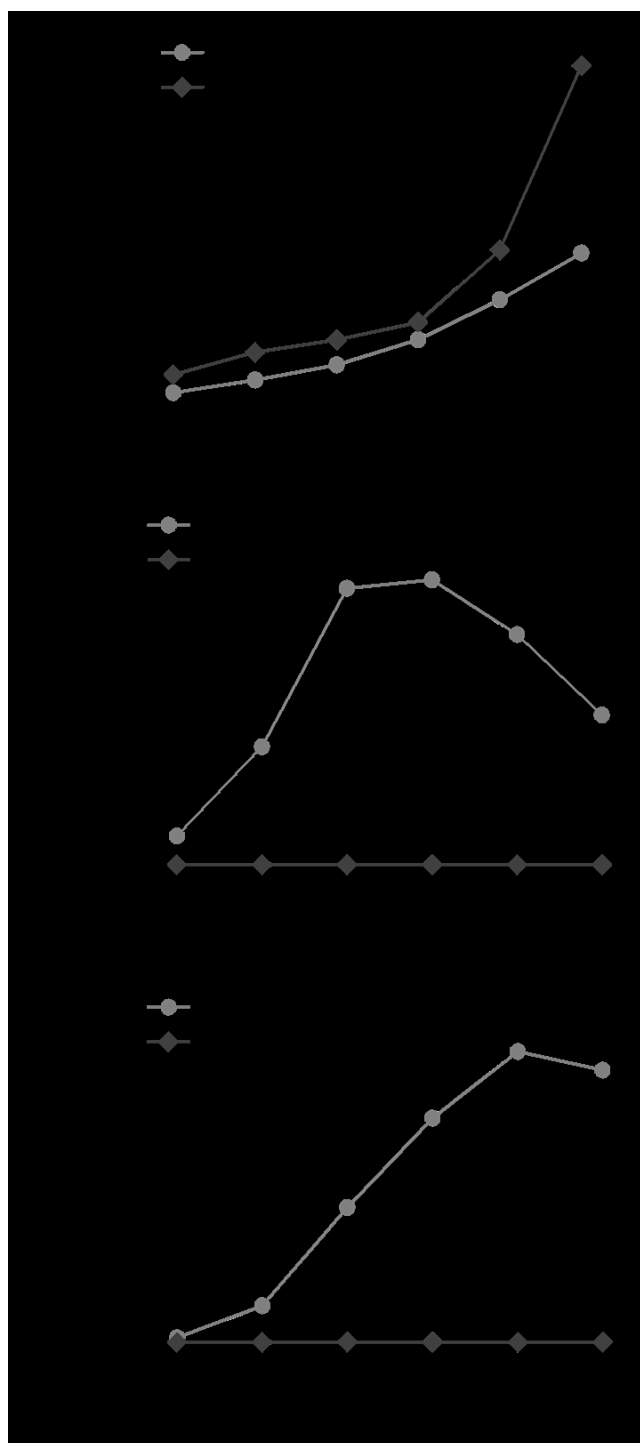


atmosphere.



**Figure 4.** CO production rate vs. volume fraction of O<sub>2</sub> in the O<sub>2</sub>/CO<sub>2</sub> part of the feed gas (CO<sub>2</sub>, N<sub>2</sub> and O<sub>2</sub>) with PIM or PIM/aniline as the CO<sub>2</sub>/O<sub>2</sub> selection layer. Electrolyte: 0.5 M aqueous KHCO<sub>3</sub>; Cathode catalyst: CoPc/CNT; Anode catalyst: CoO<sub>x</sub>/CNT; Cell voltage: 3.4 V. Volume fraction of N<sub>2</sub> in the feed gas is fixed at 50%. The dash line in the graph marks the noise level. Error bars represent standard deviations from multiple measurements.

The PIM/aniline gas selection layer also allows us to produce useful liquid products from electrochemical CO<sub>2</sub> reduction in the presence of O<sub>2</sub>, which has never been realized before. To generate formate, we used Sn metal particles as the cathode catalyst<sup>30</sup> and performed electrolysis in a three-electrode cell with enhanced gas diffusion (see Supporting Information). With 5% O<sub>2</sub> in the feed gas, the control Sn electrode without PIM/aniline exhibits a  $j_{\text{total}}$  up to 295.0 mA/cm<sup>2</sup> (**Figure 5a**) but produces no formate (**Figure 5b** and **5c**) at various electrode potentials. This is because O<sub>2</sub> reduction completely dominates the catalyst surface, in consistency with our previous observation.<sup>10</sup> In sharp contrast, the electrode with PIM/aniline as the gas selection layer can catalyze CO<sub>2</sub> reduction to formate with a FE close to 100% and a  $j_{\text{formate}}$  of 56.7 mA/cm<sup>2</sup> at a cathode potential of -2.4 V vs Ag/AgCl, despite the presence of 5% O<sub>2</sub>. As the electrode potential is further polarized to -2.8 V,  $j_{\text{formate}}$  increases to 73.6 mA/cm<sup>2</sup>.



**Figure 5.** (a) Total current density, (b) formate FE, and (c) formate partial current density at various cathode potentials (without  $iR$  correction). There is 5%  $O_2$  in the  $CO_2$  feed gas. Electrolyte: 0.5 M aqueous  $KHCO_3$ ; Cathode catalyst: Sn; Anode catalyst: NiFe-layered double hydroxide.

In summary, we have developed a  $CO_2$ -selective layer by introducing aniline into the pores of

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PIM and revealed that the acid-base interaction between CO<sub>2</sub> and aniline enhances CO<sub>2</sub> separation from O<sub>2</sub>. Loaded with CO<sub>2</sub> reduction electrocatalysts, the PIM/aniline catalytic electrodes show improved O<sub>2</sub> tolerance. CO<sub>2</sub> in a feed gas with an O<sub>2</sub>/CO<sub>2</sub> ratio as high as 9:1 can be effectively reduced to CO. Formate can be produced at a near-unity FE and a high current density from electrochemical CO<sub>2</sub> reduction in the presence of O<sub>2</sub>. The strategy of introducing chemical sieving to a gas separation membrane could be useful for directly mining the atmospheric CO<sub>2</sub> for fuels.

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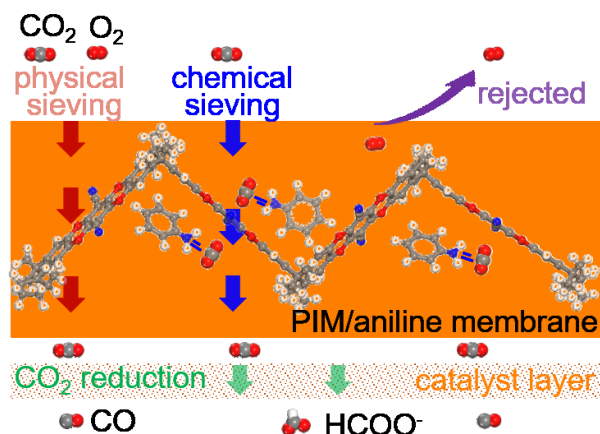
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## TOC figure and text



An aniline-infiltrated polymer-of-intrinsic-microporosity (PIM) membrane is reported for direct valorization of CO<sub>2</sub> from its mixture with O<sub>2</sub>. The acid-base interaction between CO<sub>2</sub> and aniline enhances CO<sub>2</sub>/O<sub>2</sub> separation, enabling catalytic electrodes capable of producing CO from a feed gas with an O<sub>2</sub>/CO<sub>2</sub> ratio as high as 9:1 and of reducing CO<sub>2</sub> selectively to formate in the presence of O<sub>2</sub>.