

# ***Supporting Information***

## **Electrochemical Reduction of Gaseous CO<sub>2</sub> at Low-Intermediate Temperatures using a Solid Acid Membrane Cell**

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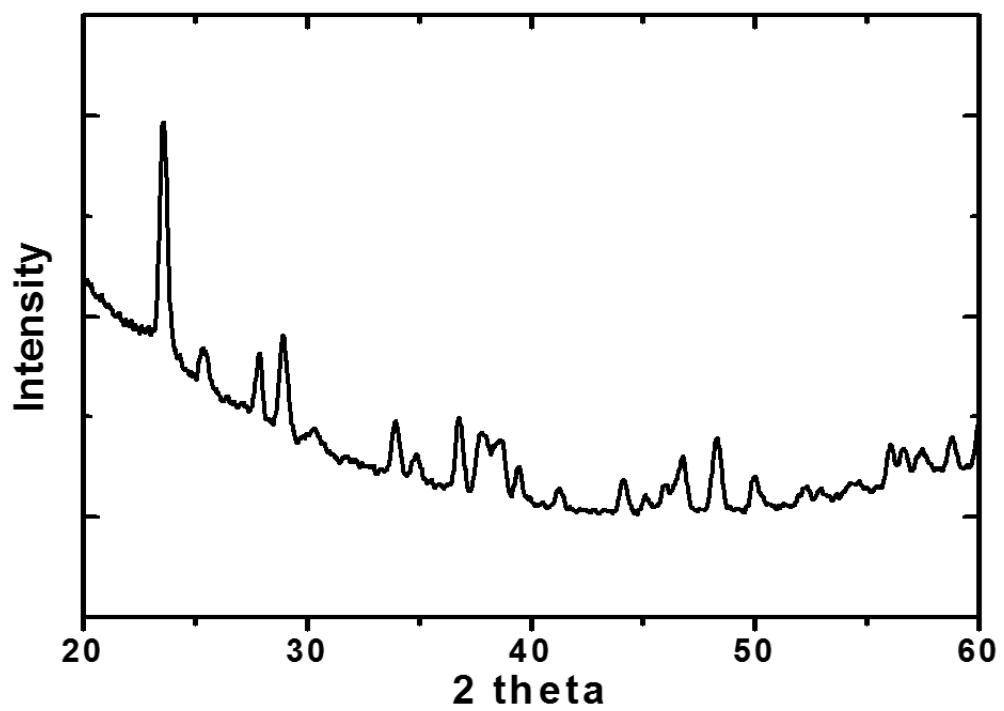
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**Table S1.** Composition of the mixture to be deposited on the carbon paper to fabricate the Pt-based or Cu-based electrode for the membrane-electrode assembly (MEA) with  $\text{CsH}_2\text{PO}_4$ . Pt (<20  $\mu\text{m}$ , Sigma-Aldrich, Product #: 205915) and Cu (14–25  $\mu\text{m}$ , Sigma-Aldrich, Product #: 326453) were used as the electrocatalysts.

Pt-based	Cu-based
Pt powder <20 $\mu\text{m}$ (Aldrich) 0.4 mg/cm <sup>2</sup>	Cu powder 14–25 $\mu\text{m}$ (Aldrich) 0.4 mg/cm <sup>2</sup>
+	+
$\text{CsH}_2\text{PO}_4$ powder (synthesized) 1.2 mg/cm <sup>2</sup>	$\text{CsH}_2\text{PO}_4$ powder (synthesized) 1.2 mg/cm <sup>2</sup>
+	+
2-propanol 3 mL/cm <sup>2</sup>	2-propanol 3 mL/cm <sup>2</sup>

**Table S2.** Number of electrons to produce one molecule of each product via CO<sub>2</sub> reduction.

<b>CO<sub>2</sub> reduction products</b>	<b># of electrons to produce one molecule of the product via CO<sub>2</sub> reduction</b>
CO	CO <sub>2</sub> + 2H <sup>+</sup> + <u>2e<sup>-</sup></u> → CO + H <sub>2</sub> O
CH <sub>4</sub>	CO <sub>2</sub> + 8H <sup>+</sup> + <u>8e<sup>-</sup></u> → CH <sub>4</sub> + 2H <sub>2</sub> O
C <sub>2</sub> H <sub>6</sub>	2CO <sub>2</sub> + 14H <sup>+</sup> + <u>14e<sup>-</sup></u> → C <sub>2</sub> H <sub>6</sub> + 4H <sub>2</sub> O
C <sub>2</sub> H <sub>4</sub>	2CO <sub>2</sub> + 12H <sup>+</sup> + <u>12e<sup>-</sup></u> → C <sub>2</sub> H <sub>4</sub> + 4H <sub>2</sub> O
C <sub>2</sub> H <sub>2</sub>	2CO <sub>2</sub> + 10H <sup>+</sup> + <u>10e<sup>-</sup></u> → C <sub>2</sub> H <sub>2</sub> + 4H <sub>2</sub> O
CH <sub>3</sub> OH	CO <sub>2</sub> + 6H <sup>+</sup> + <u>6e<sup>-</sup></u> → CH <sub>3</sub> OH + H <sub>2</sub> O
HCOOH	CO <sub>2</sub> + 2H <sup>+</sup> + <u>2e<sup>-</sup></u> → HCOOH



**Figure S1.** X-ray diffraction pattern of the synthesized  $\text{CsH}_2\text{PO}_4$ .

**Table S3.** Produced concentration [ $\mu\text{mol}/\text{cm}^2$ ] and Faradaic efficiency (F.E. [%]) of the products from the electrochemical reduction of gaseous  $\text{CO}_2$  with the Pt-CsH<sub>2</sub>PO<sub>4</sub>-Cu MEA.

[ $\mu\text{mol}$ ] F.E. [%]	CO	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>	CH <sub>3</sub> OH	HCOOH
0 min		-	-	-	-	-	-
10 min	0.38 <b>0.12</b>	0.18 <b>0.23</b>	0.009 <b>0.020</b>		-	-	-
40 min	1.9 <b>0.15</b>	0.81 <b>0.26</b>	0.027 <b>0.015</b>		-	0.036 <b>0.009</b>	0.009 <b>0.001</b>
70 min	2.6 <b>0.12</b>	1.7 <b>0.30</b>	0.054 <b>0.017</b>		-	0.080 <b>0.011</b>	0.018 <b>0.001</b>
100 min	3.0 <b>0.10</b>	2.5 <b>0.32</b>	0.089 <b>0.020</b>	0.009 <b>0.002</b>	0.009 <b>0.001</b>	0.13 <b>0.012</b>	0.027 <b>0.001</b>
130 min	3.5 <b>0.09</b>	3.3 <b>0.32</b>	0.12 <b>0.020</b>	0.018 <b>0.003</b>	0.018 <b>0.002</b>	0.16 <b>0.012</b>	0.036 <b>0.001</b>

Initial gas composition in the cathode chamber: 5400  $\mu\text{mol}$   $\text{CO}_2$ , 2100  $\mu\text{mol}$   $\text{H}_2\text{O}$

Test conditions: Pt/CsH<sub>2</sub>PO<sub>4</sub>/Cu (surface area: 1  $\text{cm}^2$ )

-2 V,  $\text{H}_2/\text{CO}_2$  (0.4 atm  $\text{H}_2\text{O}$  both), 250°C

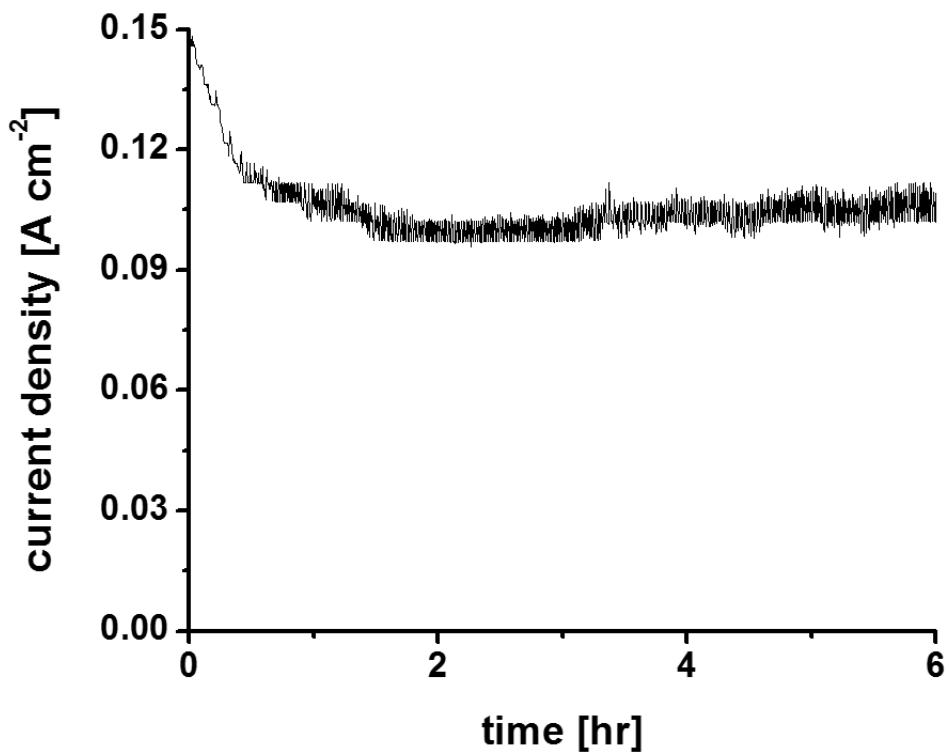
**Table S4.** Produced concentration [ $\mu\text{mol}/\text{cm}^2$ ] and Faradaic efficiency (F.E. [%]) of the products from the electrochemical reduction of gaseous  $\text{CO}_2$  with the Pt-CsH<sub>2</sub>PO<sub>4</sub>-Pt MEA.

[ $\mu\text{mol}$ ] F.E. [%]	CO	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>	CH <sub>3</sub> OH	HCOOH
0 min		-	-	-	-	-	-
10 min	0.47 <b>0.15</b>	0.018 <b>0.023</b>	-	-	-	-	-
40 min	2.2 <b>0.18</b>	0.089 <b>0.028</b>	-	-	-	-	-
70 min	3.9 <b>0.18</b>	0.18 <b>0.033</b>	0.009 <b>0.003</b>	-	-	-	-
100 min	5.3 <b>0.17</b>	0.31 <b>0.040</b>	0.018 <b>0.004</b>	-	-	-	-
130 min	6.3 <b>0.15</b>	0.44 <b>0.040</b>	0.018 <b>0.003</b>	-	-	-	-

Initial gas composition in the cathode chamber: 5400  $\mu\text{mol}$   $\text{CO}_2$ , 2100  $\mu\text{mol}$   $\text{H}_2\text{O}$

Test conditions: Pt/CsH<sub>2</sub>PO<sub>4</sub>/Pt (surface area: 1  $\text{cm}^2$ )

-2 V,  $\text{H}_2/\text{CO}_2$  (0.4 atm  $\text{H}_2\text{O}$  both), 250°C



**Figure S2.** Current density-time curve for the Pt/CsH<sub>2</sub>PO<sub>4</sub>/Cu with -2 V constant cell voltage for the time duration during which CO<sub>2</sub> is being electrochemically reduced.