Electrochemical CO_2 Reduction to Ethylene Glycol at only 200 mV Overpotential on Iron Phosphide

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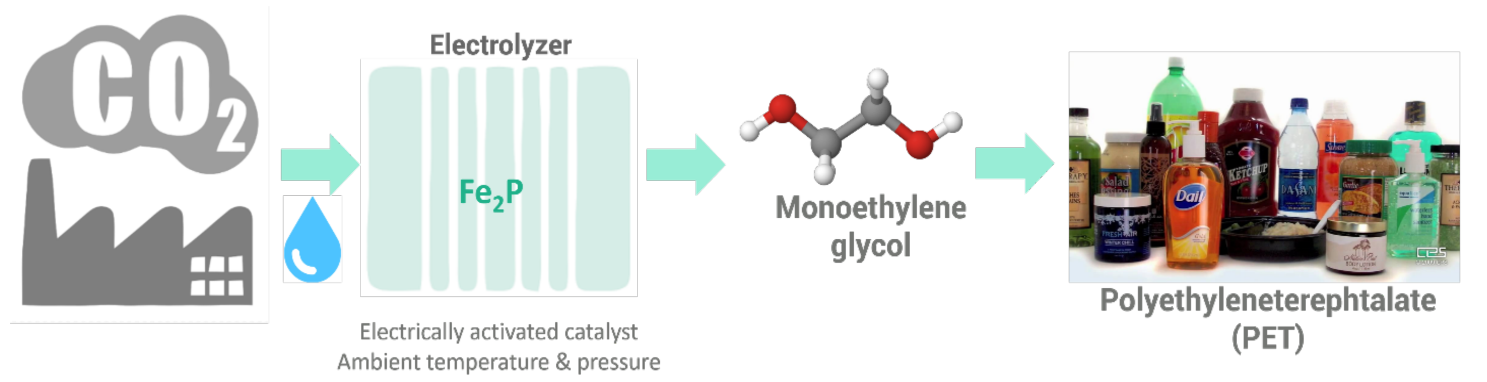
Introduction

CO_2 reduction involves the conversion of exhaust CO_2 into value-added chemicals. It is widely believed to be one of the most promising technologies for minimizing CO_2 emissions into the atmosphere, and for slowing the rate of global warming. We are proposing the earth-abundant transition metal phosphide catalyst, Fe_2P as an efficient catalyst to convert CO_2 to valuable chemical monomers.

Our study has found that Fe_2P has the ability to convert CO_2 into:

- Ethylene glycol- a valuable monomer for the formation of PET
- Methylglyoxal- a substitute for urea-formaldehyde resins
- 2,3-Furandiol- a highly reactive aromatic ring

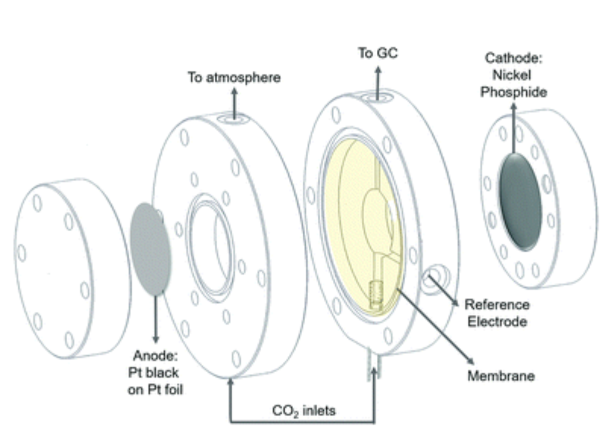


The CO_2 Reduction Reaction

$2\,H_2O + 2\,e^- \rightarrow H_2 + 2OH^-$	$E^0 = 0V$
$CO_2 + 2\,(e^- + H^+) \rightarrow$ formic acid	$E^0 = -0.02$ V
$2\,CO_2 + 10\,(e^- + H^+) \rightarrow 2\,H_2O +$ ethylene glycol	$E^0 = +0.20$ V
$3\,CO_2 + 12\,(e^- + H^+) \rightarrow 4\,H_2O +$ methylglyoxal	$E^0 = +0.02$ V
$4\,CO_2 + 14\,(e^- + H^+) \rightarrow 5\,H_2O +$ 2,3-furandiol	$E^0 = +0.01$ V

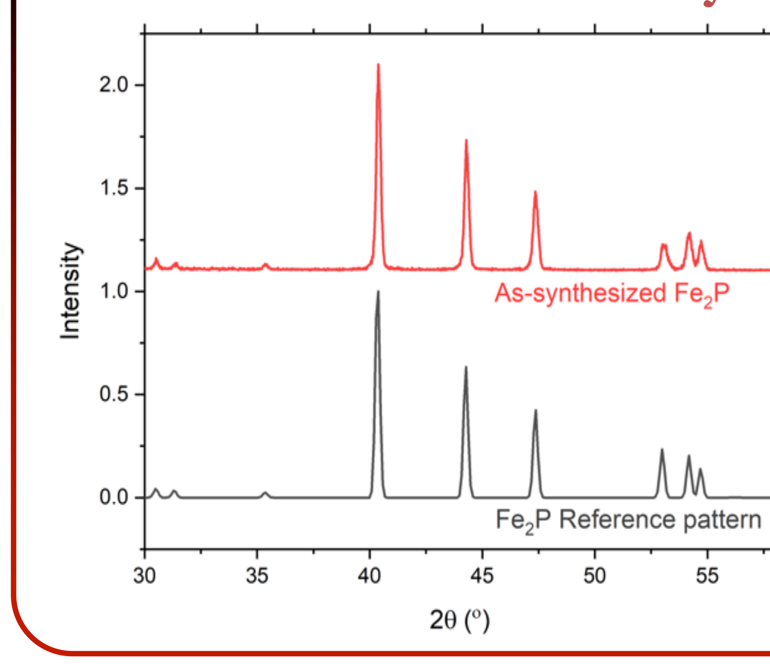
Electrode preparation

Electrochemical Cell



CO_2 is bubbled through the bottom to ensure saturation. The cell has a large catalyst surface area to volume ratio (3.14 cm^2 vs 6 mL per side) to maximize reaction rate. Liquid products are tested via HPLC and NMR, and gas products via gas chromatography.

Purity of As-Synthesized Fe_2P

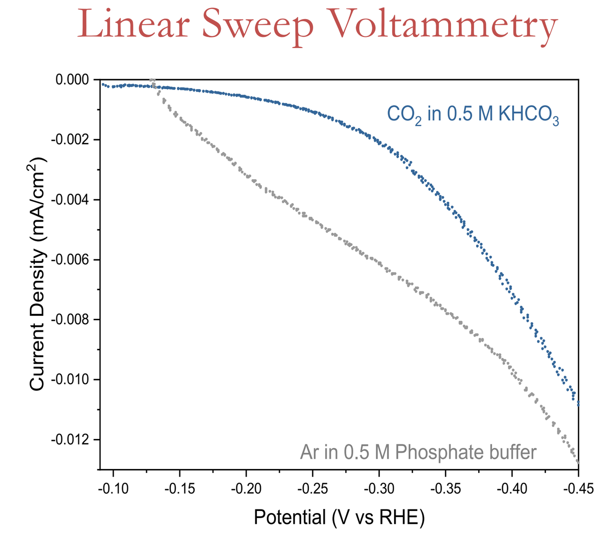


Powder X-Ray Diffraction spectroscopy of the as-synthesized Fe_2P powders (left) are compared to the Fe_2P reference pattern and show that the Fe_2P is phase-pure within the 2% detection limit.

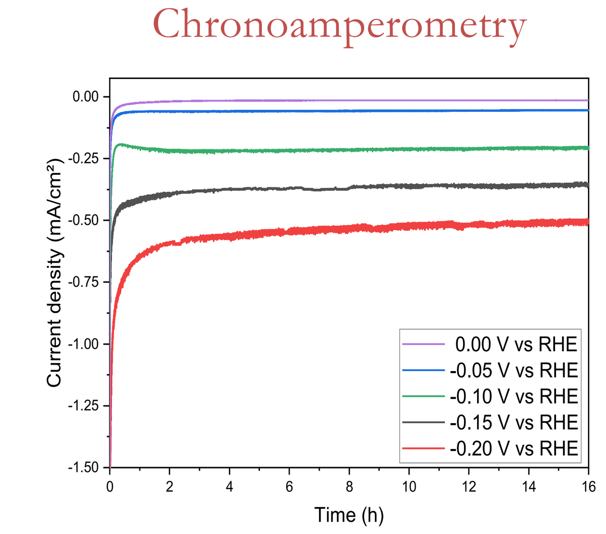
The homogeneity of the Fe_2P phase was also confirmed by scanning electron microscope and X-ray photoelectron spectroscopy.

LSV and Chronoamperometry

Linear Sweep Voltammetry



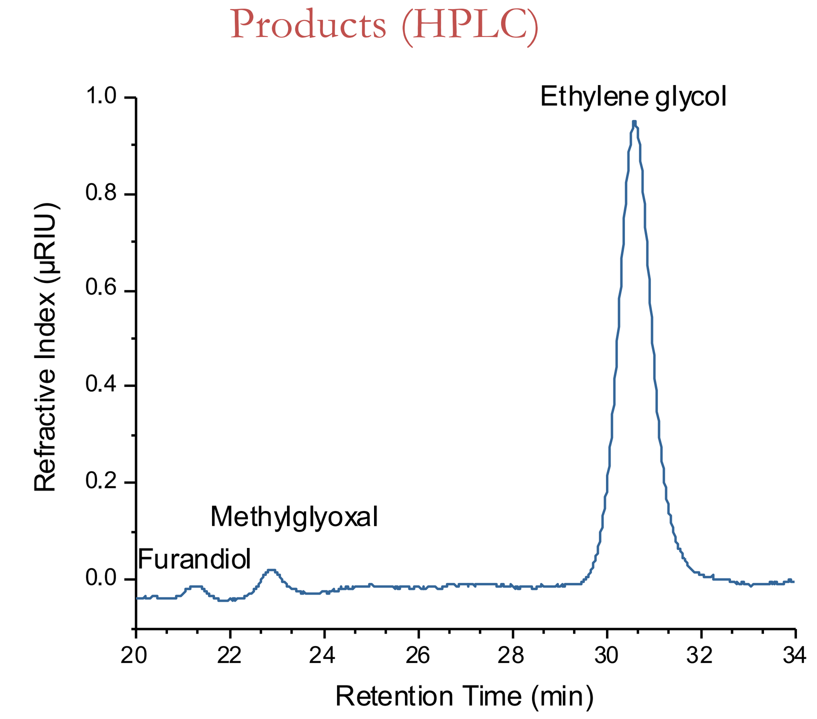
Chronoamperometry



LSV indicates that the CO_2RR and HER reaction compete with each other for active sites. Chronoamperometry was conducted at five overpotentials, with current density increasing as overpotential increased.

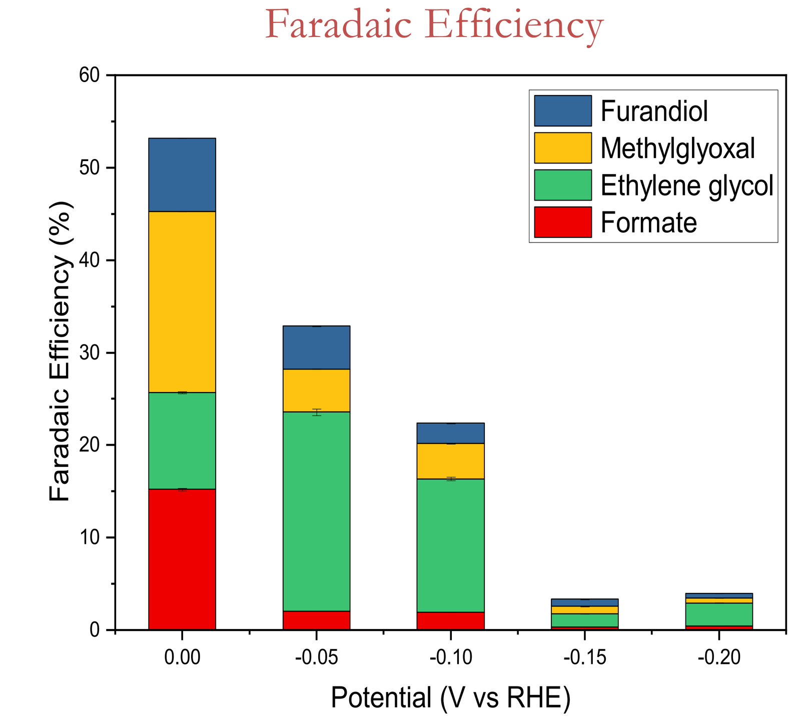
Faradaic Efficiency and Current Density

Products (HPLC)



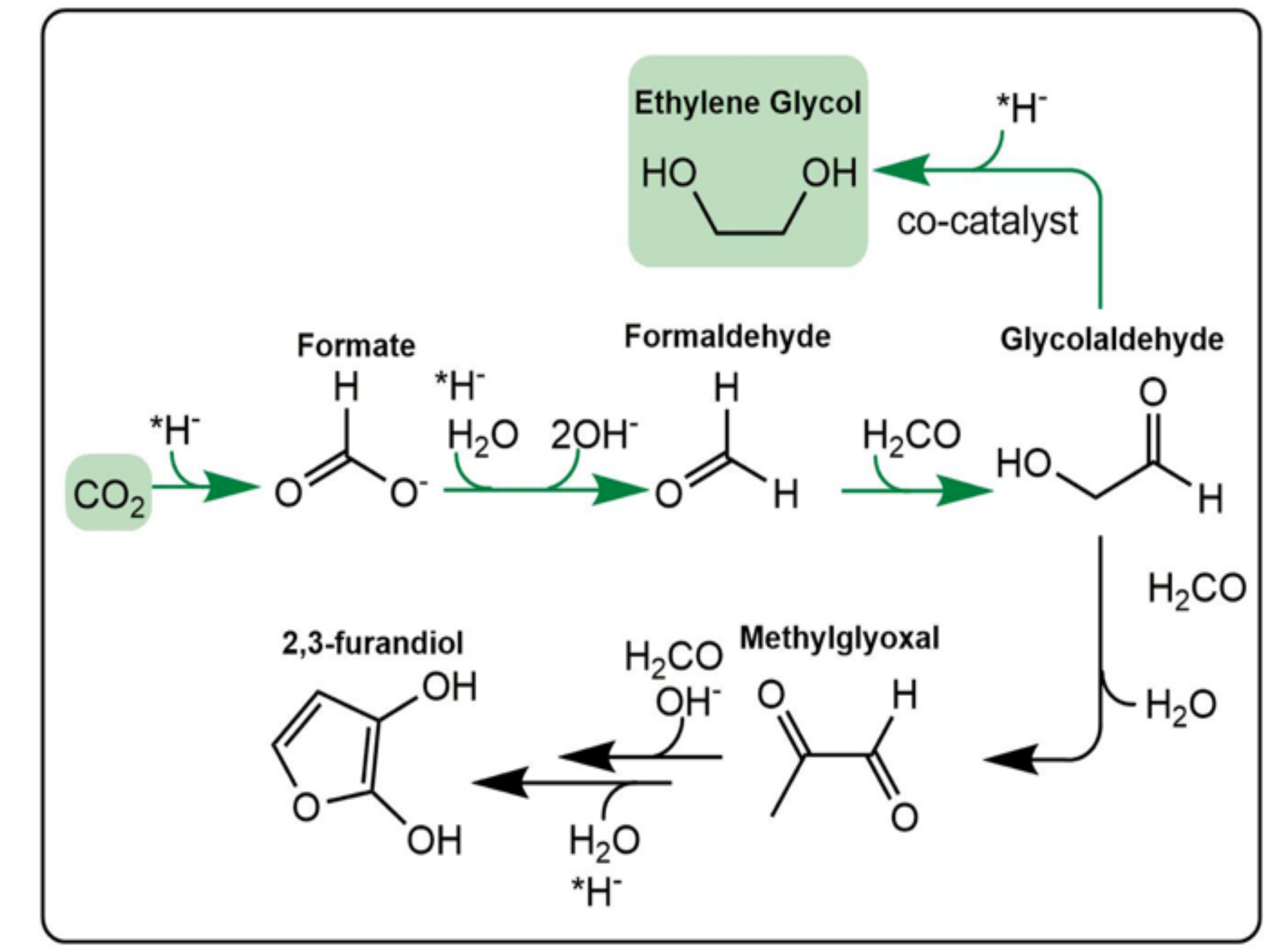
HPLC was used to identify the liquid CO_2 reduction products. The main product is ethylene glycol, which has not been produced by any of our previous catalysts, Ni_2P and Cu3P.

Faradaic Efficiency



FE highest at 0 V vs RHE with 53% FE for CO_2RR. As overpotential is increased, CO_2RR FE decreases but ethylene glycol FE increases, with a maximum of 22% FE for ethylene glycol at -0.05 V vs RHE. Maximum selectivity for ethylene glycol is 65% and occurs at -0.05 and -0.1 V vs RHE.

Proposed Formation Mechanism



Unlike the previous transition metal catalyst, such as Ni_2P, the Fe_2P results in ethylene glycol formation. This is believed to be because the Fe-P bond on the surface adatom P layer is stronger than the Ni-P bond, resulting in lower chances for the adatom P to bridge with neighboring active sites. Thus, less C-C coupling results before the molecule is released back into solution.

Conclusions

- Synthesized phase-pure Fe_2P via solid-state synthesis method
- Maximum CO_2RR FE of 53% at 0 V vs RHE
- 22% FE for ethylene glycol production at -0.05 V vs RHE
- High selectivity for ethylene glycol on Fe_2P, with 65% selectivity at -0.05 and -0.1 V vs RHE
- First transition metal catalyst which produces ethylene glycol at low overpotentials and with substantial FE

Acknowledgements

I would like to thank the amazing people of the Dismukes group who I have been fortunate enough to work with over the past three years: Karin, Anders, and Dr. Dismukes. I am grateful that they decided to take a chance on my 17-year old self, and I hope that it paid off for them; I know it has for me. I would also like to thank Rutgers for giving me the opportunity to join this group via the Aresty program. Being a part of this group has made me the scientist that I am today, and resulted in me being able to pursue my PhD at Stanford University in the field that I love.

Calvinho, Karin U. D., Anders B. Laursen, et al. 2018. "Selective CO_2 Reduction to C_3 and C_4 Oxyhydrocarbons on Nickel Phosphides at Overpotentials as Low as 10 mV." *Energy & Environmental Science*. The Royal Society of Chemistry. doi:10.1039/C8EE00936H.

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