

3D-Printing of Porous Electrodes for Electrochemical CO₂ Reduction

4TU.Energy **TUDelft**

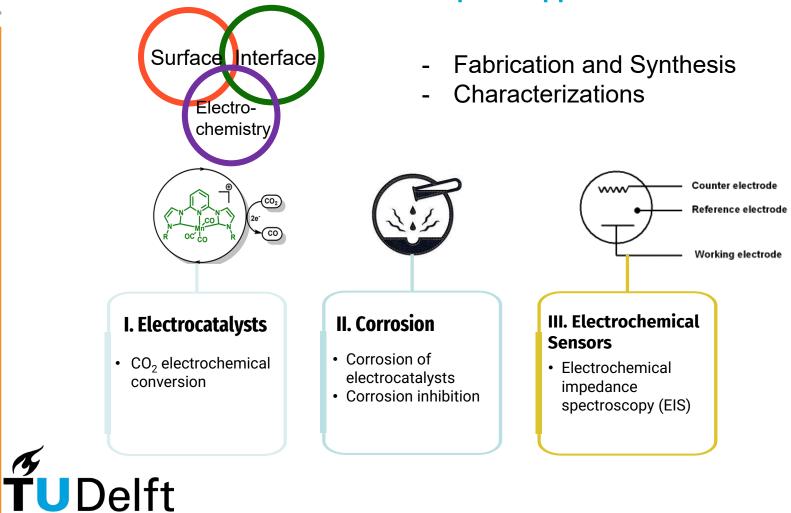
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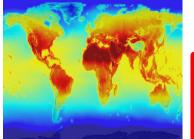


Research Concepts & Applications





CO₂ - Climate change!













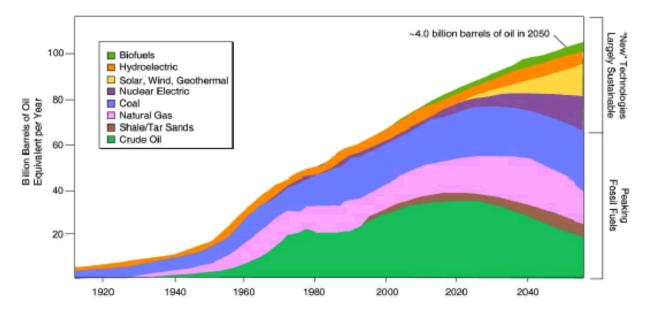






Long-term global energy generation

World Energy Demand—Long-Term Energy Sources

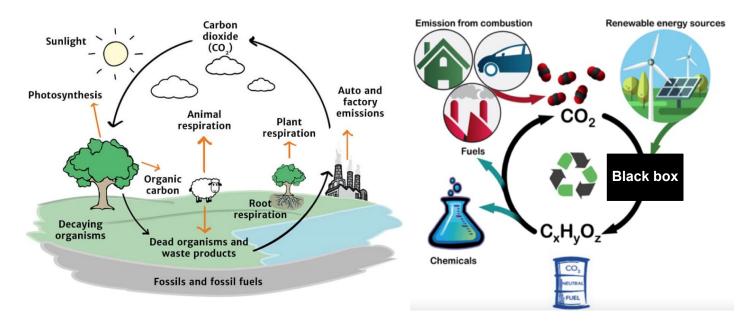


Sources: Lynn Orr, Changing the World's Energy Systems, Stanford University Global Climate & Energy Project (after John Edwards, American Association of Petroleum Geologists); SRI Consulting.



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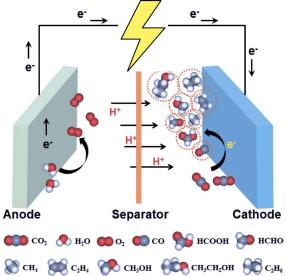
"Carbon Cycle" Let's learn from the nature!



 $6CO_2 + 6H_2O + energy \rightarrow C_6H_{12}O_6 + 6O_2$



The black box: Electrocatalysts





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Reduction: $CO_2+2H^++2e^- \rightleftharpoons CO+H_2O$



Compatative reduction: $2H_2O+2e^- \rightleftharpoons H_2+2OH^-$

Oxidation: $2H_2O \rightleftharpoons O_2+4H^++4e^-$

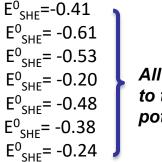
Zhang et al., Adv. Sci. (2018) 5, 1700275.

Thermodynamic & Kinetic Considerations

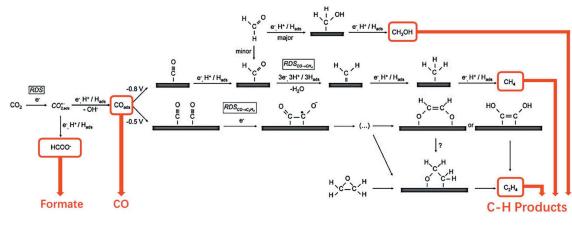
Y. Hori, electrochemical CO₂ reduction on metal electrodes, Modern Applications of Electrochemical Technology, No42, Springer, NY (2008).

 $2H^{+} + 2e \rightarrow H_{2}$ $CO_{2} + 2H^{+} + 2e \rightarrow HCOOH$ $CO_{2} + 2H^{+} + 2e \rightarrow CO + H_{2}O$ $CO_{2} + 4H^{+} + 4e \rightarrow C + 2H_{2}O$ $CO_{2} + 4H^{+} + 4e \rightarrow HCHO + H_{2}O$ $CO_{2} + 6H^{+} + 6e \rightarrow CH_{3}OH + H_{2}O$ $CO_{2} + 8H^{+} + 8e \rightarrow CH_{4} + 2H_{2}O$

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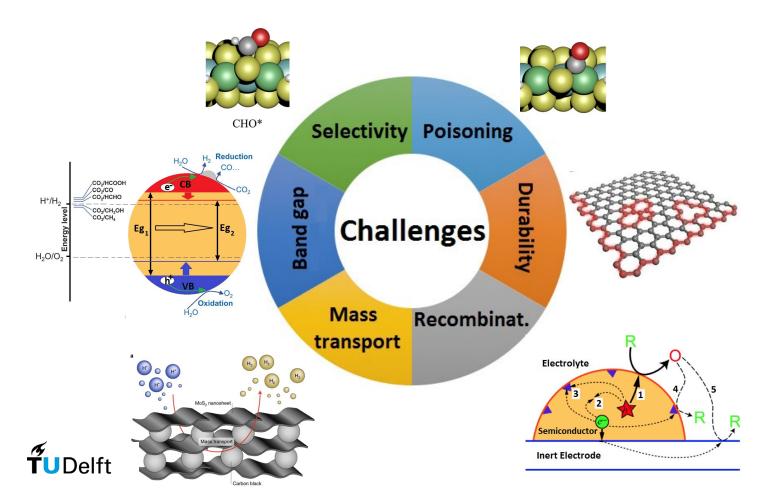


All values are close to the H₂ evolution potential

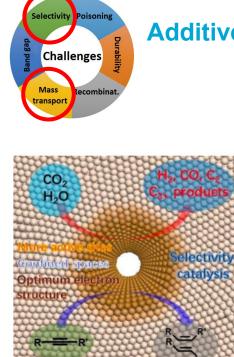


Yin, et al. Trends in Chemistry, November, Vol. 1, No. 8

Practical Challenges



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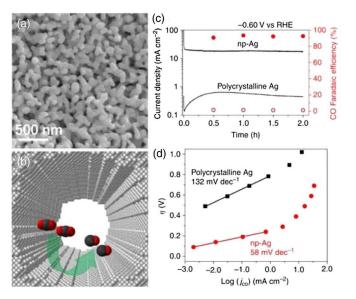


Porous Metal Nanocrystalline Catalysts

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Additive Manufacturing to Enhance CO₂ RR Efficiency

Min et al, CCS Chem. 2022, 4, 1829–1842.



Lu et al. F. A Selective and Efficient Electrocatalystfor Carbon Dioxide Reduction.Nat. Commun.2014,5, 3242.

- Confined spaces increase the retention time of key intermediates to promote the selective catalysis.
- An increased surface area improves the
- Precise manufacturing of pore size and structure is a value offered by additive manufacturing!





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Objectives:

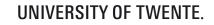
- Fabrication of porous electrode with improved catalytic performance through the sophisticated precise tuning of interconnected hierarchical pore sizes.
- Combine 3D printing techniques with tailored functional coating to improve the current/power densities of CO₂ electrochemical conversion.
- Fundamental understanding of the impact of material architecture on overall faradaic efficiency, in particular mass transfer limitations.









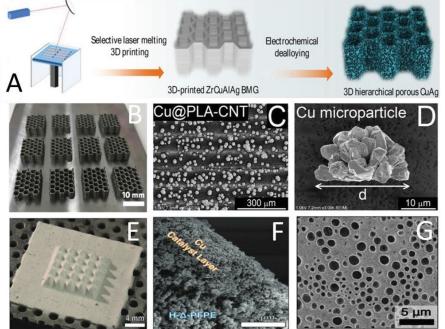




The advantages of 3D-printed systems for CO₂ reduction:

- Complex geometry and distribution control
- Versatility in design
- Scalability and reproducibility
- Minimal waste production
- Cost-effectiveness

TUDelf⁺



Padinjareveetilet et al., Advanced Materials Interfaces 10.8 (2023): 2201734





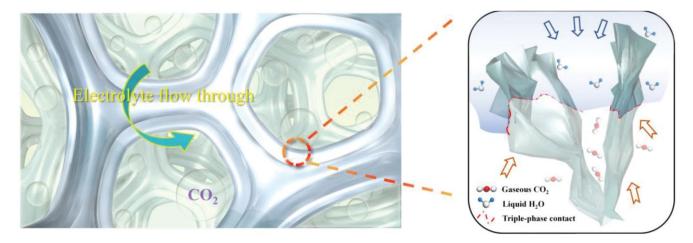
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The merits of porous electrode for CO₂ reduction:



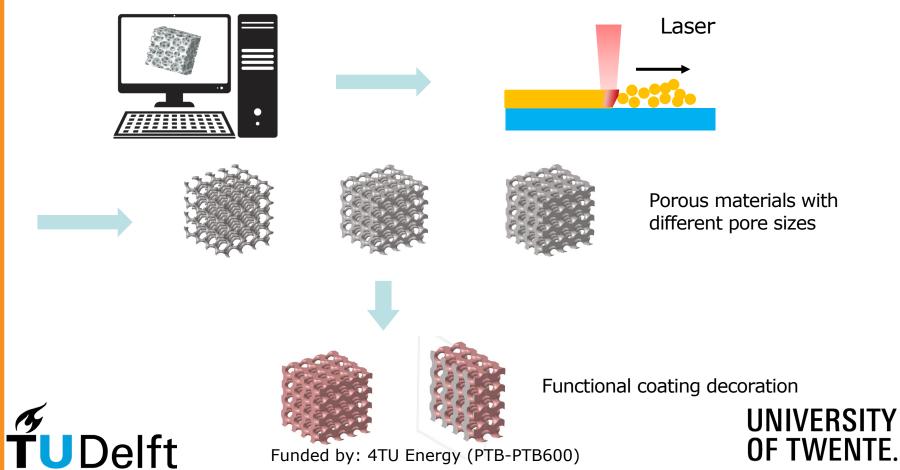
Shi et al., Advanced Science 9.30 (2022): 2204472.

- ✤ improved the selectivity for CO₂ reduction,
- increased specific surface area for reactions,
- improved mass transfer properties,
- Reduced overpotential and energy efficiency.

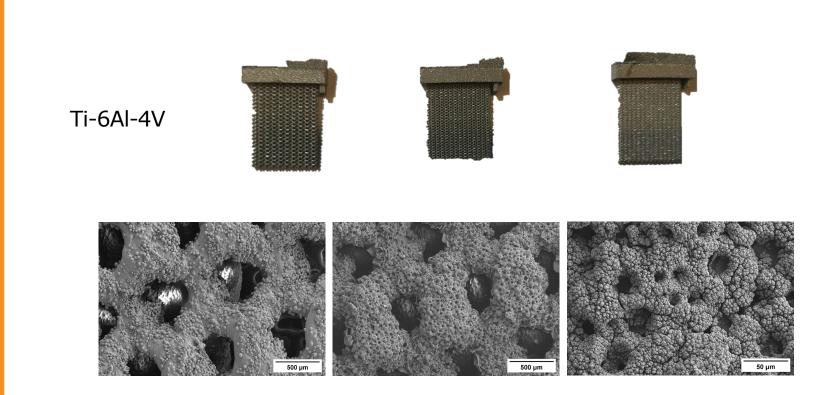


4TU. Fabrication of porous substrate

Laser Powder Bed Fusion: LPBF



4TU. Fabrication of different porous sizes



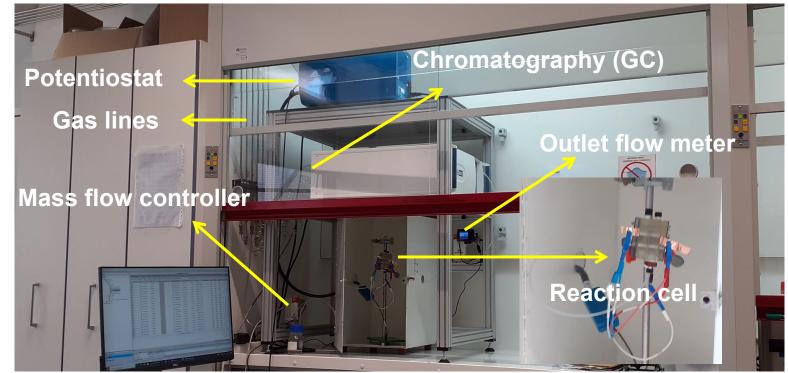






Lab-scale Reactor







Funded by: 4TU Energy (PTB-PTB600)

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Summary & Next Steps

- Deposition of Copper (Cu) nanoparticles onto porous Ti alloybased substrates through electroless deposition.
- Elucidating the impact of varying **pore size** on the efficiency and resultant products of CO₂ reduction.
- Understanding the effects of pore size and co-catalysts on the product selectivity.





Thank you for your attention!

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Materials Science and Engineering