*Cat 2*   *Cat 2*

Cat 1

Exploration of Electrode Geometry on Tandem Cascade Catalysis for CO$_2$ reduction (CO$_2$R) to methanol

Enhancing the performance of heterogeneous electrochemical cascades by adjusting electrode geometry to improve diffusional mass-transport in aqueous buffered systems.

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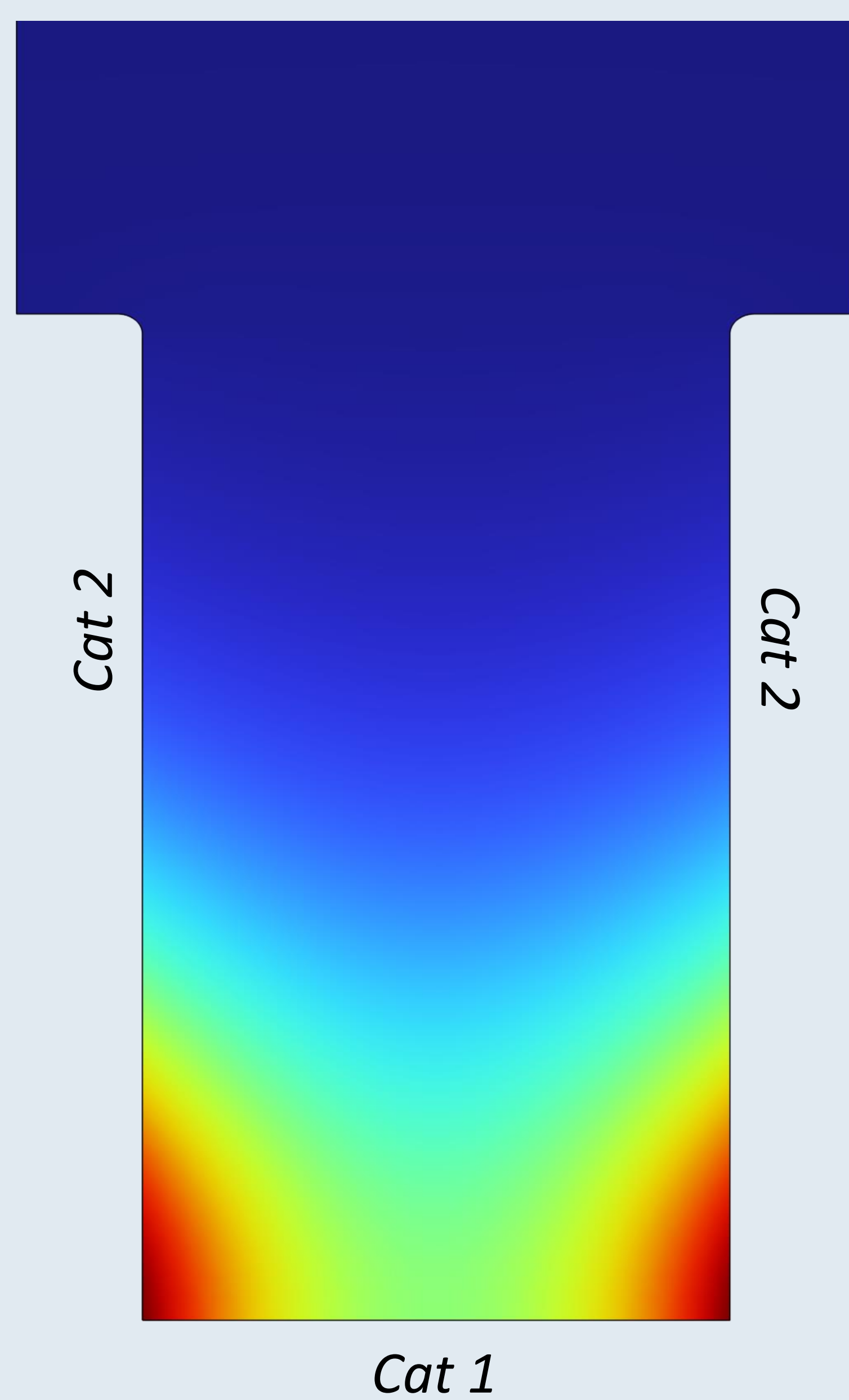
Abstract

Electrochemical CO$_2$R cascades holds promise for converting CO$_2$ to fuels and chemicals. We developed a generalized steady-state simulation in which the catalysts are patterned on a periodic trench design. This geometry is hypothesized to be able to yield a higher net current density for a CO$_2$R cascade reaction. We investigate the role of geometry on mass transport, local microenvironments, and selectivity for a model CO$_2$R cascade reaction.

The model considers local concentration gradients of bicarbonate species at quasi-equilibrium and the parasitic hydrogen evolution reaction (HER). *Our results suggest that varying the spatial distribution of active sites plays a significant role in facilitating effective mass-transport between active sites and modulating selectivity*. Moreover, we observe that this trench geometry significantly alters the cascade reaction rate by affecting the local pH.
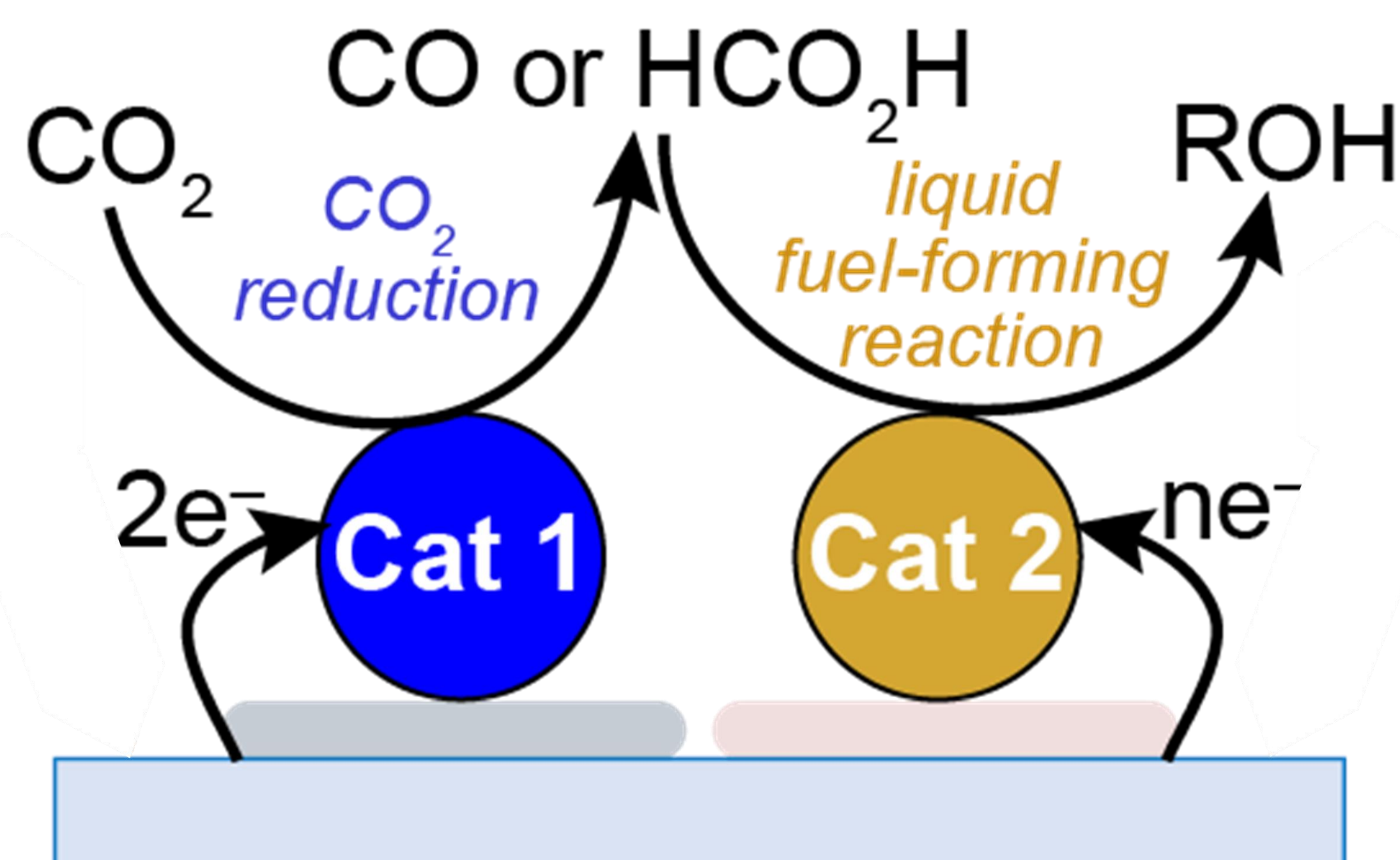
Figure 1: Diagram of tandem electrochemical cascade catalysis for CO$_2$ reduction to value-added products

Methodology

A half-cell catalyst surface is modeled in 2D for a CO$_2$ reduction cascade in a bicarbonate buffer. Periodic boundary conditions are used to capture the repeating architectures. The **1st catalyst** is located on the basal plane, while the **2nd catalyst** is located on the remaining electrode trench surfaces.

Electrode kinetics are governed using the concentration-dependent Butler-Volmer equation:

$$i_{loc} = i_0 \left(C_R exp \left(\frac{\alpha_a F \eta}{RT} \right) - C_O exp \left(\frac{-\alpha_c F \eta}{RT} \right) \right)$$

Results

- With the modeled catalyst configuration and kinetics, increasing trench depth reaches a maximum pH of 8 at ~ 100 μm and stabilizes as the trench depth increases.

- Angled-closed (confined) trenches perform better than angled-out (open) trenches for tandem catalysis. This is due to the confined trench geometry increasing local alkalinity within the trench and partially suppressing HER.
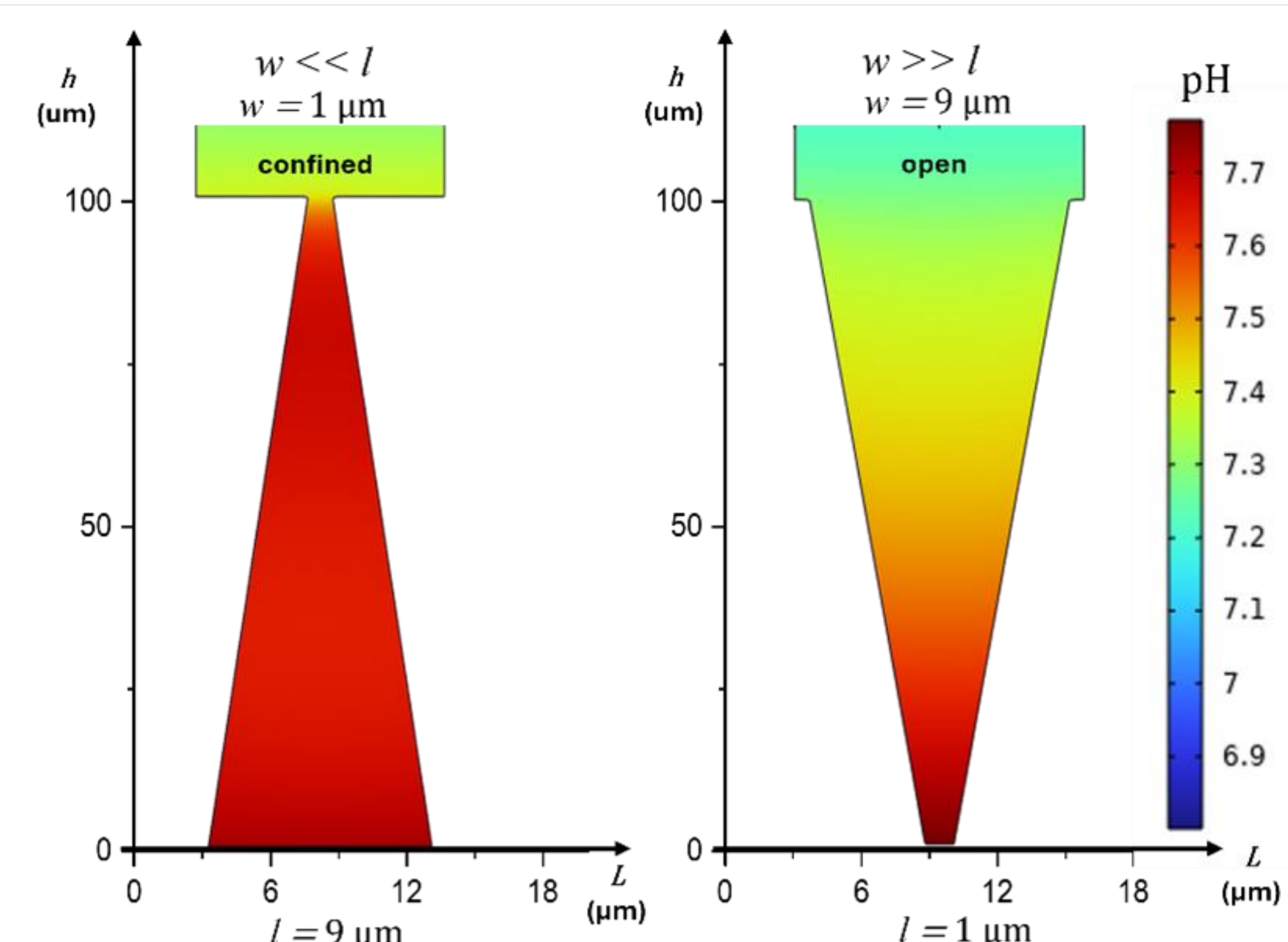

Figure 2: Steady-state pH profiles for the confined (left) and open (right) trench geometries. Cat 1 is located at the bottom. Cat 2 is located on the trench walls.

REFERENCES

M. García-Batlle, P. Fernandez, C. Sheehan, S. He, T. E. Malllouk, G.N. Parsons, J. F. Cahoon, R. Lopez "Spatially Patterned Architectures to Modulate CO2 Reduction Cascade Catalysis Kinetics." Publication submitted to *ACS Catalysis* (2024)

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