Magic at the interface: a microfabrication-based approach to study multicomponent CO_2 reduction catalysts

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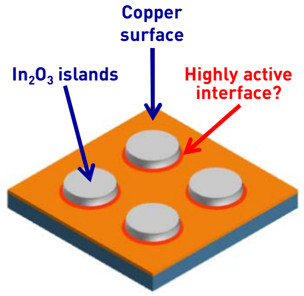
Introduction

- Combining the **electrochemical reduction of CO_2** (eCO_2RR) with renewable energy sources is an attractive approach for converting carbon emissions into **fuels and chemicals**.
- In particular, reducing **CO_2 to CO** would provide a versatile building block for the production of **liquid fuels** and **plastics** by well-established processes in **industry**.
- The emergence of **synergistic effects** in **multicomponent catalysts** may **break the scaling relations** that limit the performance of pure **transition metal surfaces**.[1]
- **Indium-modified catalysts** have shown **high selectivity** for the **reduction of CO_2 to CO** at decreased overpotentials.[2, 3]



- The **high selectivity toward CO** of copper-indium catalysts was first attributed to a **HER-inhibiting effect** from **indium** in **alloys** formed under reaction conditions (e.g., $Cu_{11}In_9$).[2]
- However, our previous studies with **Ag-In**[4] and **Cu-In**[5] catalysts revealed a **synergistic interaction** between **metallic components** and **oxidic indium phases**, suggesting that **highly active sites** at **metal-oxide interfaces** might be responsible for the enhanced performance of indium-modified catalysts.
- In this work, we developed a **new experimental approach** based on **microfabricated model electrodes** (tested under conventional **eCO_2RR conditions**) to gain insights into the **identity of the active phases** and the **role of interfaces** in copper-indium catalysts.[6]

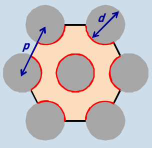
Results and Discussion

Microfabrication of model electrodes

We **initially hypothesized** the the synergistic effect observed in **Cu-In catalysts** was due to the existence of **highly active sites** at the **interfaces between In_2O_3 and metallic Cu**. We further reasoned that, **if this premise is true**, we would observe a **direct relationship** between the **CO evolution activity** and the **length of these interfaces**.

Therefore, we searched for a **synthetic procedure** that provided a **high degree of control** over the **catalyst composition and structure** and produced **large electrodes** suitable for testing over **conventional eCO_2RR conditions** with **accurate quantification of products**.

Distribution of oxide islands



Hexagonal lattice

Each electrode comprises a **regular array** of well-defined islands on the surface.

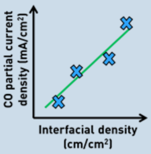
Indium oxide islands are grey
Copper surface is orange
Interfacial perimeter is red

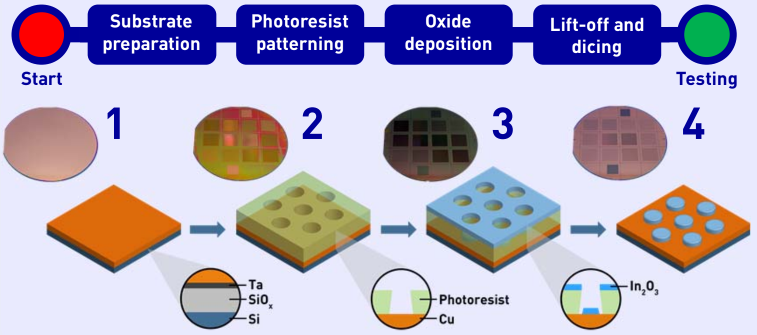
The arrangement is defined by the **pitch** and the **diameter** of the oxide islands.

Interfacial density and active sites

$$\text{Interfacial density (ID)} = \frac{\text{Total perimeter of oxide islands on surface}}{\text{Electrode area}}$$

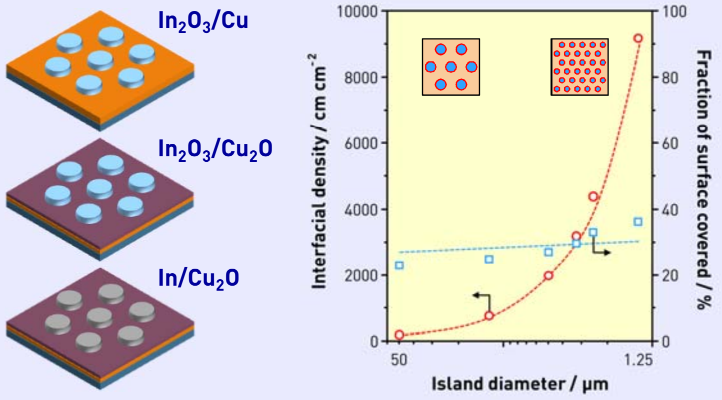
Although the actual **quantity of interfacial sites** is unknown, we reasoned that this figure should be **proportional** to **the contact perimeter** of the islands.





Cu or Cu_2O is **sputtered** on a **4-inch silicon wafer** followed by **UV photolithography** using a **negative photoresist**. In_2O_3 is deposited by **electron beam evaporation**, and the photoresist is finally lifted-off by dipping in NMP. Twelve electrodes (two for each geometry) and the corresponding single-phase controls are obtained from each wafer after dicing, demonstrating the **high throughput** of the process.

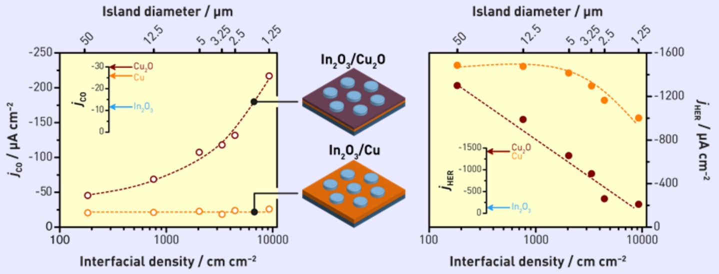
Compositional and geometrical control



We evaluated **three different island/substrate compositions**. In terms of geometry, the **interfacial density** of the electrodes **varies across two orders of magnitude** while the **single-phase coverage** aims to keep a **constant contribution from non-interfacial sites**.

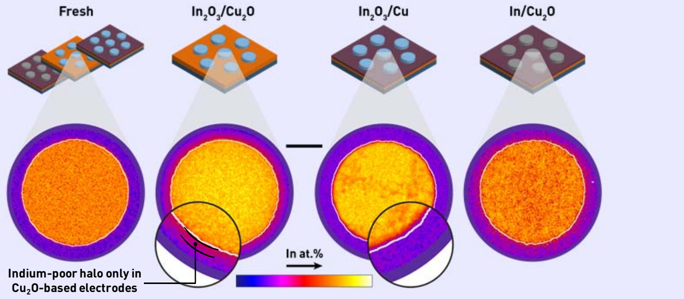
Catalytic activity and the role of interfaces

CO and hydrogen evolution activity at −0.6 V vs. RHE (0.1 M $KHCO_3$, pH 6.8)



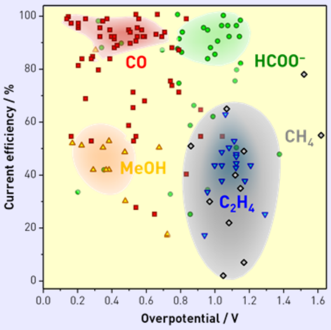
CO evolution activity depends strongly on the **interfacial density** only over **In_2O_3/Cu_2O** and **In/Cu_2O** electrodes. This indicates that **oxidic indium is not important**, but that the **presence of Cu_2O** (which is reduced to Cu under reaction conditions) **in contact with an indium source** is necessary for the **synergistic effect** to occur.

Pre- and post-reaction elemental distribution by SEM-EDX



Elemental mapping revealed **indium diffusion** into the **copper substrate** upon the **reduction of Cu_2O under reaction conditions**. The **halos** around the islands correspond to **indium-modified copper surfaces** (metallic at eCO_2RR potentials) which are the **likely source of the high CO evolution performance of Cu-In catalysts**.

A few thoughts on the way ahead



Great progress in CO_2 reduction to CO and, to a lesser extent, to $HCOO^-$. However, **efficiently targeting multicarbon products remains a major challenge.**[1]

Because **CO is a key intermediate** on the way to multicarbon products, it makes sense to focus on **CO electroreduction**. We can think about using **different catalysts for each step**.

However, **in contrast to the eCO_2RR**, besides copper (and oxide-derived copper) very **few materials and strategies** have been explored **for reducing CO to more complex products**.

What catalyst design strategies can we use to increase the rate of carbon-carbon coupling in CO electroreduction? Can multicomponent catalysts (e.g., alloys) break the stalemate?

References: [1] G.O. Larrazábal, A.J. Martín, J. Pérez-Ramírez *J. Phys. Chem. Lett.* **2017**, 8, 3933 [2] S. Rasul, D.H. Anjum, A. Jedidi, Y. Minenkov, L. Cavallo, K. Takanabe *Angew. Chem. Int. Ed.*, **2015**, 54, 2146 [3] G.O. Larrazábal, A.J. Martín, F. Krumeich, R. Hauert, J. Pérez-Ramírez *ChemSusChem* **2017**, 10, 6, 1255 [4] G.O. Larrazábal, A.J. Martín, S. Mitchell, R. Hauert, J. Pérez-Ramírez *J. Catal.* **2016**, 343, 266 [5] G.O. Larrazábal, A.J. Martín, S. Mitchell, R. Hauert, J. Pérez-Ramírez *ACS Catal.* **2016** 6, 6265 [6] G.O. Larrazábal, T. Shinagawa, A.J. Martín, J. Pérez-Ramírez *Nat. Commun.* **2018**, 1477

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