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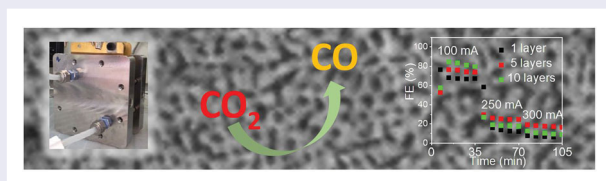
Electrochemical CO₂ to CO reduction at high current densities using a nanoporous gold catalyst

Zhen Qi^a, Monika M. Biener^a, Ajay R. Kashi^b, Sara Hunegnaw^b, Alvin Leung^b, Sichao Ma^b, Ziyang Huo^b, Kendra P. Kuhl^b and Juergen Biener^a

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ABSTRACT

We report on integrating ultrathin monolithic nanoporous gold (npAu) catalyst coatings for CO₂ reduction in a large electrode area (25 cm²) electrochemical membrane reactor with gas diffusion electrodes at 100 mA/cm². The CO Faraday efficiency increases with increasing thickness, from 65% to 75% and 80% for 1, 5, and 10 layers of npAu leaves where each npAu leaf layer is 100 nm thick. For the one npAu leaf layer configuration, this corresponds to an extremely high CO current density of 955 A/g gold thus demonstrating the potential for commercial applications.



IMPACT STATEMENT

By device level optimization of catalyst integration we significantly improved the utilization of gold catalysts for electrochemical CO₂ reduction to syngas at industrial relevant current densities of 100 mA/cm².

ARTICLE HISTORY

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KEYWORDS

electrochemical CO₂ reduction; nanoporous gold; dealloying; electrocatalyst; gas diffusion electrode

Introduction

With rapidly decreasing prices for renewable electrical energy, electrochemical CO₂ reduction (CO₂R) is becoming a promising technology for generating carbon neutral fuels and chemicals [1]. For example, syngas, a mixture of CO, H₂, and CO₂ that is used as feedstock for the Fischer–Tropsch process, can be generated by CO₂R [2]. CO₂R also provides a pathway for high-volume seasonal energy storage by transforming the electrical energy produced by intermittent renewable energy sources, such as wind and solar, into chemical energy. However, the development and integration of scalable, low-cost, reactive, and selective electrocatalysts for these transformations remains a challenge. For the electrochemical CO₂ to CO reduction, noble metal catalysts such as Au have shown good catalytic reactivity with almost 100% selectivity but require further optimization

in catalysts utilization to offset the high costs of noble metal catalysts.

Nanoporous gold (npAu) has been shown to exhibit high selectivity for the CO₂ to CO conversion [3,4]. The material is prepared by a process called dealloying, that is, selective corrosion of the less noble components of an alloy which in the case of npAu typically is Ag from a Ag–Au alloy. The low solubility (34 mM) and slow diffusion kinetics of CO₂ in aqueous electrolytes [5] leads to depletion of the reactant CO₂ while simultaneously changing the pH value at the catalyst surface [6] which together limit the achievable current density. Pushing the technology towards industrial applications requires the use of large area state-of-the-art electrochemical membrane reactors (ECMRs) with gas diffusion electrodes like those used in fuel cells. Even though the concentration of CO₂ in the humidified gaseous phase is similar to that of a CO₂

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saturated aqueous electrolyte, the four orders of magnitude higher diffusivity of CO₂ gas (16 mm²/s) compared to CO₂ in aqueous solution (0.0016 mm²/s) [5] effectively eliminates CO₂ depletion at the catalyst surface thus opening the door to the realization of industry-relevant high current densities. For example, Jhong *et al.* [7] demonstrated CO₂R current densities of close to 100 mA/cm² and Faradaic efficiencies (FEs) up to 95% at ~3 V cell potential using a membraneless electrolyzer design with one square centimeter gas diffusion electrodes and a Ag catalyst loading of 0.75 mg/cm². Not surprisingly, more and more CO₂R studies are performed in gas diffusion ECMRs [5,8].

In the present work, we use a one-step dealloying method to integrate 100-nm-thick npAu leaf catalysts into 25 cm² gas diffusion electrodes of a state-of-the-art zero-gap electrochemical membrane reactor (ECMR) and studied the effect of catalyst loading and integration on the CO₂R performance. The zero-gap ECMR is an ideal candidate for combining high current densities with high energy efficiency as the absence of liquid electrolytes minimizes cell resistance [9]. We demonstrate that the monolithic nanoporous morphology of npAu leaf catalyst enables industry-relevant current densities of 100 mA/cm² at cell potentials as low as 2.2 V by facilitating mass and electronic transport.

Experimental

Preparation and integration of the npAu leaf catalyst

Monolithic 100-nm-thick npAu leaves (3–3/8" × 3–3/8") were prepared from 12 K (Au_{0.35}Ag_{0.65}) white gold leaf (Gold Leaf Company) by floating them on concentrated HNO₃ (10 ml) in a petri dish. For 100 nm thick gold leaf, complete leaching of the Ag content (65 vol%) takes only 1 h at room temperature, leaving behind nanoporous gold with its characteristic bicontinuous ligament-pore structure with 65% porosity [10]. After the dealloying process, the acid was completely but slowly exchanged against DI water. The resulting monolithic npAu leaf, still floating on top of the DI water, was rinsed for at least three more times with DI water. Next, a 25 cm² carbon paper gas diffusion layer (GDL) (Sigracet, BC 39) was carefully inserted underneath the floating npAu leaf which was then transferred to the GDL by slowly removing the residual DI water. For higher npAu catalyst loadings multiple npAu leaves (5 or 10) were stacked on top of each other before the dealloying process. For spray coating, the npAu leaves were collected in a glass vial (20 ml) filled with DI water and broken up into a few micron wide and 100 nm thick flakes using a Sonic Dismembrator. The

GDL carbon paper was then spray coated with a mixture of the resulting npAu leaf flakes with isopropyl alcohol (IPA) and ionomer.

Materials characterizations

SEM images were collected using a field-emission SEM (Jeol 7410) with lower secondary electron detector, an accelerating voltage of 5 keV and a working distance of 8 mm. The STEM images were taken with the same SEM but a different sample holder with an accelerating voltage of 30 keV.

Electrochemical CO₂ reduction testing

The npAu leaf-GDL cathode assemblies were integrated into a 25 cm² Opus 12 Inc zero-gap gas diffusion ECMR using an Orion Polymer BN2™ alkaline exchange membrane (AEM) to separate the npAu cathode-GDL assembly from the IrO_x-coated porous Ti anode. The cathode-AEM-anode assembly was compressed between two flow fields against the respective cell current collectors. CO₂ gas was directly fed into the cathode side of the electrolyzer at a flow rate of 250 sccm maintaining a cell pressure of 10 psi, while 0.5 M KOH was circulated via a peristaltic pump on the anode side at a rate of 60 mL/min. Electrolysis was run in constant current mode with 35-minute holds at 100, 250, and 300 mA/cm². The as-generated gas products were detected by GC with FID and TCD detectors measuring CO and H₂ yields, respectively.

Results and discussion

The npAu ligament/pore size is about 10 nm (Figure 1a,b) as dealloying of the ~100-nm-thick white gold leaf takes only one hour which greatly reduces the coarsening of the structure during dealloying. As reported in previous work, the surface area of npAu with 10 nm features is ~6 m²/g (as measured by BET and electrochemical active surface area analysis) [11]. STEM micrographs were obtained by transferring the npAu leaf onto a TEM grid. The optical image of npAu leaf (Figure 1b, inset) demonstrates the monolithic nature of this material. The bicontinuous ligament/pore morphology of npAu is ideally suited for gas diffusion electrodes as it allows for the formation of triple phase boundaries where liquid, gas, and solid meet.

After spraying with anion ionomers, the npAu leaf-GDL assembly was tested in a commercial scale electrolyzer (Figure 1c inset) with a 25 cm² electrode using a catholyteless configuration. In this work we used an anion exchange membrane as our previous

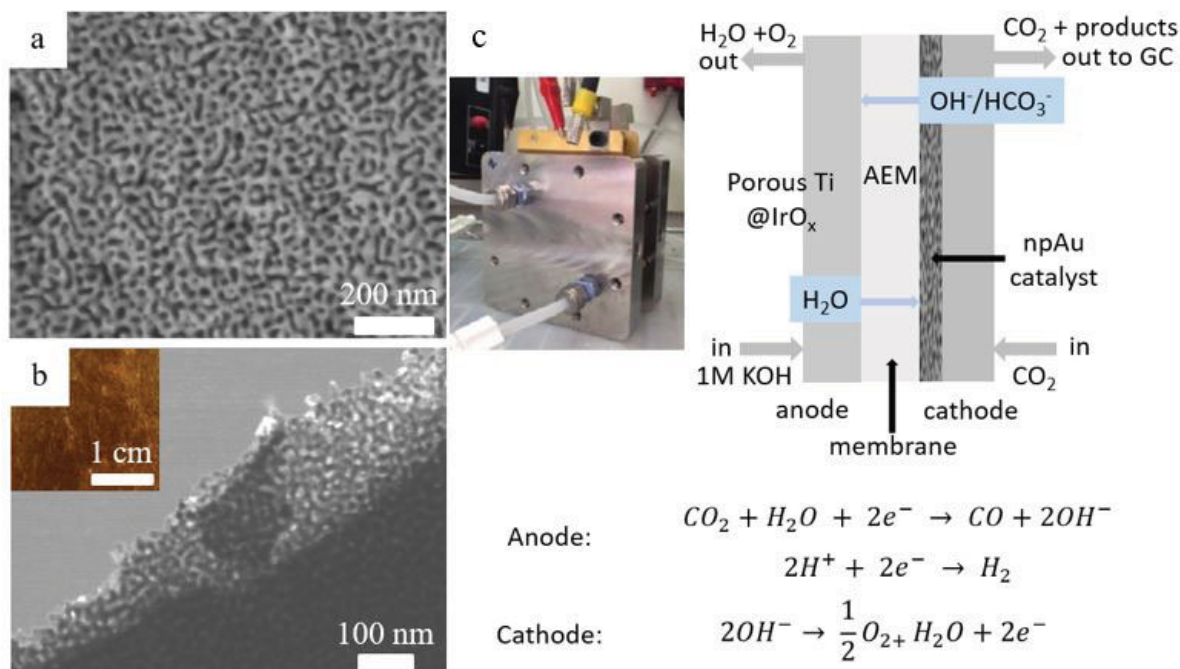


Figure 1. Microstructure of nanoporous gold leaf: (a) scanning electron microscopy (SEM) micrograph; (b) STEM image; and inset showing optical image of 100 nm thick nanoporous gold leaf showing its structural integrity. (c) Schematic diagram showing the catholyteless configuration used for electrochemical CO_2 to CO reduction in the present study and photo of a 25 cm^2 electrolyzer (inset).

CO_2R catalyst performance tests with a proton exchange membrane showed an increase of the competing hydrogen evolution reaction which we attribute to the lower pH environment in this configuration [9]. The same anion exchange chemistry was used for both the anion exchange membrane and the ionomer coating. In the gas-phase electrolyzer setup used in this work, gaseous CO_2 diffuses through the GDL and reacts on the deposited catalyst layer with water that is brought to the cathode via diffusion through the AEM from the anolyte, thus locally forming a triple phase (gas, solid, liquid) boundary at the catalyst surface. It should be noted that the cell design (Figure 1c) used in this work is optimized for gas phase products and does not allow the use of a reference electrode to measure the potential of the working electrode. Instead, the overall cell voltages are reported here.

Our experiments show that the npAu leaf catalyst exhibits a good performance towards syngas production at industry-relevant current levels of 100 mA/cm^2 . For all current densities, the overall cell voltage increases with increasing thickness of the monolithic npAu leaf catalyst (Figure 2a), for example from 2.2 V for 1-layer npAu leaf to 2.8 V for 10-layer npAu leaf @ 100 mA/cm^2 , but remains for all thicknesses stable over the testing period (each data point corresponds to 7 min). We believe that the electrical resistance increases with increasing thickness of the monolithic npAu leaf catalyst because the likelihood

of having a higher electrical contact resistance between two neighboring npAu leaf layers can be expected to increase with increasing number of layers. We believe that electron beam deposited AgAu alloy films will allow better integration of thicker npAu coatings into GDLs thus enabling a further increase in FE_{CO} .

The Faradaic efficiency (FE) of the npAu leaf catalyst for CO_2 to CO conversion is shown in Figure 2b. At 100 mA/cm^2 current density, FE_{CO} increases with the increasing number of npAu leaves loaded on the GDL support, reaching 65%, 75%, and 80% for 1, 5, and 10 layers of the npAu leaf catalyst, respectively. The 10-layer npAu sample yielded the highest CO partial current density of 80 mA/cm^2 and a cell potential of 2.8 V. Under these conditions, the rate of CO formation is 0.037 mol/h which corresponds to a CO_2 single pass conversion efficiency of 5.2%. Accounting for hydrogen evolution, the total FE is around 100% demonstrating accurate GC calibration. At higher current densities (250 and 300 mA/cm^2), the FE_{CO} decreases rapidly to less than 30% due to increased hydrogen evolution. Interestingly, the trend of increasing FE_{CO} with the increasing number of npAu leaves reverses for higher current densities, and the five-layer-thick assembly starts to outperform the 10-layer assembly.

The energy efficiency η_{EE} of the different npAu leaf catalysts was analyzed by comparing the energy of

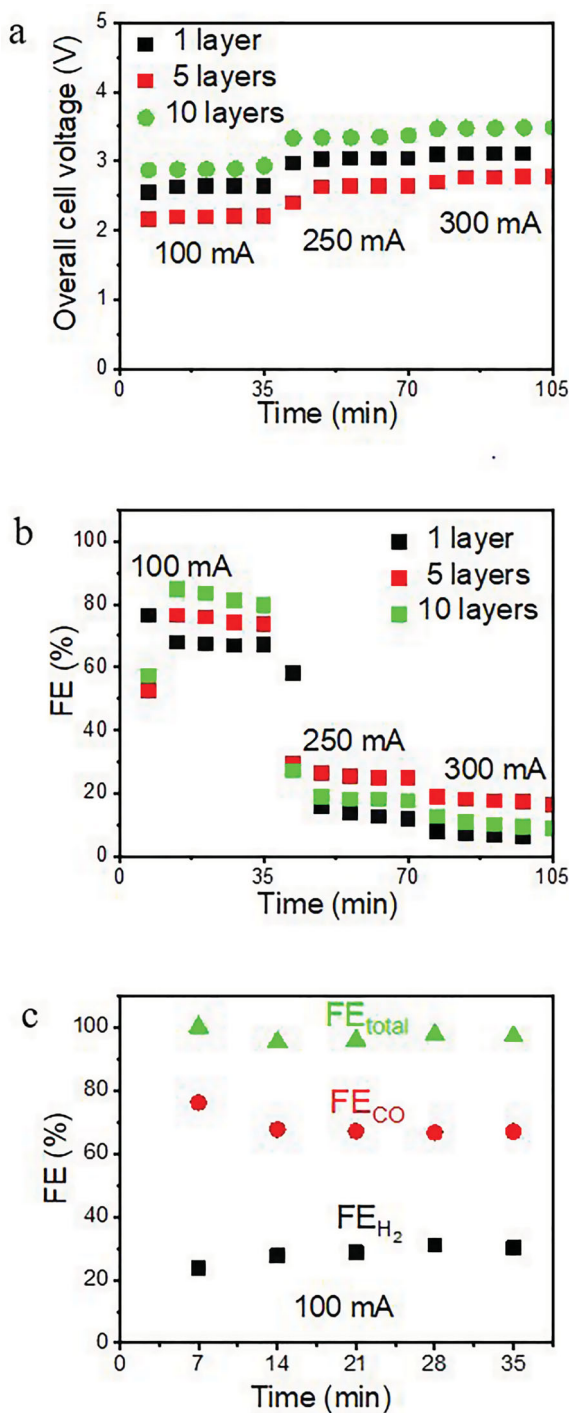


Figure 2. (a) The overall cell voltage. (b) Faraday efficiency for CO of three different layers of nanoporous gold. (c) CO, H₂, and total FE of 1 layer of nanoporous gold leaf.

reactions $\Delta_r H^0$ to the input of electrical energy:

$$\eta_{EE} = \frac{\Delta_r H^0}{E_{cell} z F}$$

$$= FE_{CO} \times \frac{\Delta_r H^0_{CO}}{E_{cell} z_{CO} F} + FE_{H_2} \times \frac{\Delta_r H^0_{H_2}}{E_{cell} z_{H_2} F} \quad (1)$$

where E_{cell} is the cell potential, z is the charge transfer number, FE are the Faradaic efficiencies, and F is the Faraday constant. Using the appropriate values for $\Delta_r H^0_{CO}$ (283 kJ/mol) and $\Delta_r H^0_{H_2}$ (286 kJ/mol) for CO and H₂ formation with oxygen evolution as the anode reaction, the measured Faradaic efficiencies and cell voltages reveals that the 1-layer npAu leaf catalyst has a total energy efficiency of 66% (considering CO formation only the efficiency is still 43%). While using 5- and 10-layer gold leaf catalyst coatings improves FE_{CO} , the energy efficiency stays constant at $\sim 42\%$ (for CO only) as the gain in FE_{CO} (from 65% for 1-layer npAu leaf to 80% for 10-layer npAu leaf @ 100 mA/cm²) is completely compensated by the accompanying increase in cell potential (from 2.2 V for 1-layer npAu leaf to 2.8 V for 10-layer npAu leaf @ 100 mA/cm²). Considering the total energy efficiency (CO + H₂), 1-layer npAu clearly outperforms 10-layer npAu leaf with 66% vs. 52%, respectively.

The 100-nm-thick npAu leaf, derived from 12 carat Ag_{0.65} Au_{0.35} alloy leaf, has a porosity of 65% resulting in a density of ~ 6.8 g/cc. For a 100-nm-thick npAu film the resulting catalyst loading is thus less than 0.06 mg/cm² resulting in a cost of ~ 0.4 cts/cm² @ a gold price of \$62/g. At a current density of 100 mA/cm² and a FE for CO₂-to-CO reduction of 65%, the gravimetric current density is 955 A/g. For 10-layer npAu leaf, the FE increases by 15% while the energy efficiency stays constant due to the increase in cell potential. But the increase in materials costs with increasing catalyst layer thickness may still make economic sense if it improves catalyst stability which will be the subject of future work. For one-layer of npAu leaf, the 65% FE for CO is right in the composition range of syngas making the present study attractive to future industrial applications generating synthetic natural gas from renewable electricity and the waste product CO₂. For comparison, the multi wall nanotube (MWNT)/pyridine-containing polybenzimidazole (poly[2,2'-(pyridine-2,6-diyl)bibenzimidazole-5,5'-diyl]) (PyPBI)/Au catalyst, which is currently the best Au catalyst for CO₂ reduction in a gas diffusion configuration [12], achieves a current density for CO of 550 A/g for the same current density. Thus, our catalyst provides a 73% improvement in gravimetric current density relative to the MWNT/PyPBI/Au catalyst. The mechanism of CO₂R on Au is well documented in the literatures, [3,13] and we attribute the excellent performance of npAu in the current electrolyzer test configuration to its morphology and ease of integration rather than a change in the reaction mechanism. While previous tests of npAu catalysts [3,4,14] in H-cells demonstrated high FEs for CO at low overpotentials but low current densities (30 mA/cm² or below), the

integration of npAu leaf catalysts in high current density gas diffusion electrolyzer designs is a critical step towards industrial applications. As stated above, previous work on Au catalysts reported FEs as high as 100%, but these experiments were performed in H-cells which limits the current density to a few mA/cm² [15,16]. It should also be noted that the testing conditions in H- and gas diffusion cells are not identical. Therefore, the performances of catalysts can be totally different because the conditions at the solid/liquid interfaces are different during the CO₂R process, for instance, pH, concentration of CO₂ at catalyst surfaces, etc.

The integration of the catalyst into the electrolyzer environment is vital to its CO₂R performance. As shown above, the monolithic bi-continuous Au ligament/pore morphology of npAu seems to enable high FE_{CO} at low cell potentials. As an alternative method, we tried spray coating of a GDL with a npAu leaf flake-based ink (Figure 3). The spray coating process generally provides good reproducibility and uniformity [7] and can easily be applied to large scale electrodes. However, this approach works best with uniform suspensions which require nanoparticles. Sonification of npAu leaf generates small, but still micron-sized npAu leaf sheets which continue to exhibit the nanoporous structure of npAu (Figure 3a) but are too large for preparing a uniform, stable suspension for ink jetting. We thus applied a hand spray technique for GDL coating (Figure 3b). The resulting catalyst coating is relatively uniform with a catalyst loading of 0.32–0.35 mg/cm². However, the roughly four times higher catalyst loading compared to single layer npAu leaf (~0.08 mg/cm²) did not result in an improved performance. While the FE_{CO} exceeded 80% at low current densities (10–20 mA/cm²), it rapidly decreased with increasing current densities (Figure 3c). At 100 mA/cm², the FE_{CO} decreased to only 30%, less than half of the FE_{CO} of even the one-layer npAu leaf GDLs (Figure 2c). The five-layer npAu leaf coating, which has the same mass loading than the spray coated npAu-GDL, achieved a FE_{CO} larger than 80%. These results clearly demonstrate that the device level CO₂ electrolyzer performance strongly depends on catalyst integration. An early study [7] on different deposition techniques for preparing gas diffusion electrodes for CO₂R supports the notion that the integration of catalysts in the GDL strongly affects its performance. Our experiments demonstrate that the monolithic npAu leaf system shows a much better performance in terms of current density, faradaic efficiency and energy efficiency than the spray coated particulate npAu leaf catalyst. The authors note that in their experience, spray-coating commercial Au nanoparticles is not a viable method for large electrode areas due to poor dispersion and thus poor coverage of the catalyst ink

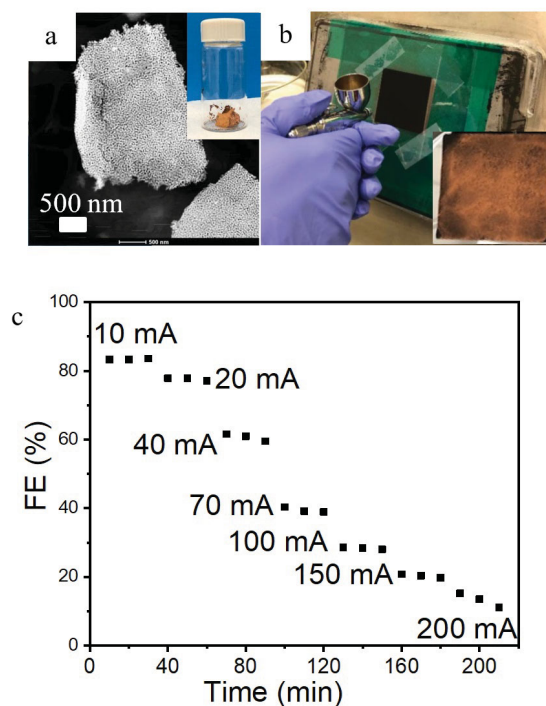


Figure 3. Nanoporous gold leaf powders: (a) STEM image showing the representative microstructure of a npAu leaf flake. Inset in (a) shows a photo of npAu leaf powder. (b) npAu leaf ink spray coating process and the inset shows an optical image of the 25 cm² gas diffusion electrode after coating. (c) Faraday efficiency for CO of npAu leaf ink-GDL assemblies with a npAu loading of 0.32–0.35 mg/cm².

slurry. The present study demonstrates that nanoporous catalysts fabricated by dealloying are suitable for commercial CO₂R electrolyzers. Our results also demonstrate the need for development of standardized testing protocols as the same catalyst with the same intrinsic activity can perform very differently depending on device integration.

In summary, we have demonstrated a facile method to integrate high surface area nanoporous gold leaf catalysts with extremely low catalyst loadings of 0.08 mg/cm² into a gas diffusion setup for effective electrochemical CO₂ reduction to syngas at industrial relevant current densities of 100 mA/cm². Maximum catalyst utilization was achieved for the one-layer npAu leaf-GDL assembly reaching a gravimetric current density of 955 A/g. We also demonstrated the importance of optimizing catalyst integration by showing that different integration of the same catalyst can dramatically change the device performance, thus underlining the need for the development of standardized testing protocols.

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Disclosure statement

A.K, S.H, A.L, S. M, Z. H, and K.K have financial interest in Opus 12, a company commercializing carbon dioxide electrolysis technology.

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