Mitigating Electrowetting in a CO_2 Electrolyzer by Using a Non-Conductive Gas Diffusion Layer

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Highlights

- Cu-mesh-based CO_2 electrolyzer was developed using metal oxides as a gas-diffusion electrode.
- The GDEs are typically based on hydrophobic carbon-based gas-diffusion layers, but they often suffer from flooding.
- Metal oxides of alumina, ceria, In-doped tin oxide, were used for gas-diffusion layer.
- Non-conductive metal oxides showed superior durability for CO_2 electrolysis due to the absence of electrowetting.

1. Introduction

Electrochemical CO_2 reduction (ECO_2R) to value-added hydrocarbons is considered as a promising technology to realize carbon neutrality. The use of gas-diffusion electrodes (GDEs) has enabled industrially relevant current densities of hundreds of mA cm^{-2} for CO_2 electrolysis. The GDEs typically consist of carbon materials, but they typically suffer from flooding. Since the flooding jeopardizes the stability of ECO_2R, we sought to understand whether this phenomenon can be eliminated by using non-conductive gas-diffusion layers (GDLs) that interface with a porous catalyst layer. In contrast with the traditional configuration of carbon-based electrodes in which a catalyst layer is deposited on a conductive GDL substrate, a Cu mesh was employed as the electron-conducting framework that was decorated with a micron-sized layer of Cu nanoparticles. This electrode was further treated on one side with a GDL based on metal oxide nanopowder (In-doped tin oxide (ITO), ceria, or alumina) mixed with PTFE (**Figure 1a and 1b**). The ECO_2R performance of these metal oxide based GDLs is contrasted with that of a Vulcan carbon (VC) GDL and studied at various current densities (–25, –50, –100, and –200 mA cm^{-2}) in an alkaline flow cell electrolyzer. Particularly, the stability of ECO_2R was measured at –200 mA cm^{-2} while observing the extent of flooding with in-situ microscopy. In combination with porosity, conductivity, and hydrophobicity data on these electrodes, the performance of an alumina-based GDL showed to avert electrowetting and assured more stable ECO_2R performance in comparison with a Vulcan carbon GDL under identical conditions.

2. Methods

GDE fabrication Cu mesh was first cut up and degreased and cleaned. Each sample was then electropolished, rinsed thoroughly, and then dried. The catalyst layer is spray-coated on one side of the Cu mesh with the catalyst dispersion to a loading of 2.1 ± 0.1 mg cm^{-2}. Then the GDL dispersion was spray-coated on top of this layer until the void space of the Cu mesh became sealed. The spray-coated sample was placed at 350 °C (above the melting point of PTFE), at which it is held for 1 h.

CO_2 electrolysis The electrolyzer was assembled with a Pt coil counter electrode (CE) inserted in the anolyte compartment, Hg|HgO reference electrode (RE) in the catholyte compartment, and Sustainion® X37-50 Grade RT membrane between the anolyte and catholyte compartments to prevent liquid product

cross-over. The current efficiencies for ECO$_2$R products were determined by gas chromatography (GC) for gas products and ^{1}H NMR for liquid products.

3. Results and discussion

Potential-induced electrolyte flooding of the GDL is a pervasive problem in ECO$_2$R that compromises the durability of the GDE as it gradually blocks the GDL pore space for CO$_2$ transport to the catalyst layer during electrolysis. We hypothesized that by employing a non-conductive but hydrophobic GDL this phenomenon of electrowetting is averted and activity and stability can be preserved even under high current density operation. Such GDLs were prepared by forming a matrix of metal oxide powder (ITO, ceria, or alumina) and PTFE and this was applied to a porous Cu-decorated Cu mesh electrode to transform the latter into a GDE. From galvanostatic electrolysis experiments in alkaline medium it was observed that with ceria- and alumina-type GDLs the selectivity reached >50 % FE for C$_{2+}$ products compared to only 22 % with a VC-type GDL. Furthermore, durability of the alumina GDL exceeded that of the VC GDL, showing stable product distribution for 10 h of uninterrupted operation at –200 mA cm^{-2}, whereas flooding of the VC GDL was imminent and detected within an hour of operation (**Figure 1c and 1d**). We reason on the basis of characterization and ECO$_2$R performance data that this is due to differences in electrical conductivity between these GDL materials, being orders of magnitude lower for the alumina material, and thereby avoids potential-induced wetting of the latter to maintain a gas transport pathway of CO$_2$ to the catalyst layer.
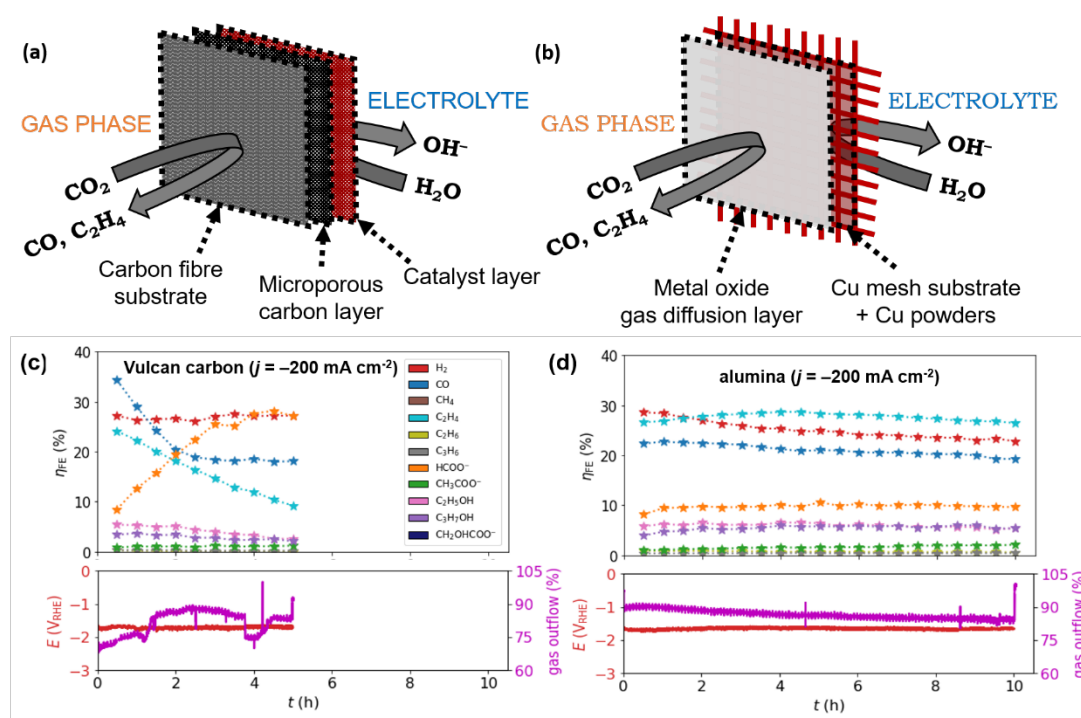
Figure 1. Schematics of (a) a typical carbon paper-based GDE and (b) a Cu mesh-based GDE. Faradaic efficiencies, cathodic potential, and gas outflow from the cell during the durability test for (c) Vulcan carbon and (d) alumina GDL.

4. Conclusions

This work shows how the choice of material properties for the gas-diffusion medium can markedly influence the product spectrum and stability of GDEs for ECO$_2$R. It provides an original perspective on the use of alternative GDL compositions toward more durable performance.