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Minor Product Polymerization Causes Failure of High-Current CO₂ to Ethylene Electrolyzers

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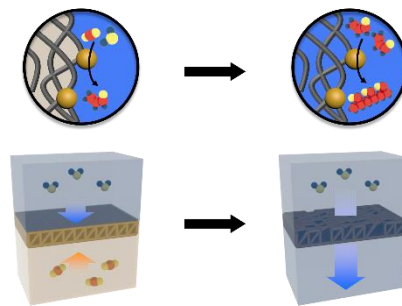
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ABSTRACT

Flooding of gas diffusion electrodes (GDEs) used in electrochemical conversion of CO₂ to ethylene is caused by polymerization of minor products. The polymer so created reduces the hydrophobicity of the GDE, leading initially to a reduction in the ethylene yield and finally to complete failure.

TOC GRAPHICS

Flooding Mechanism for Gas Diffusion Electrode



The lifetime of current GDEs used for low temperature CO₂ electrolysis is nowhere close to the parameters needed for industrialization: with target stability >20 000 h at current density >250 mA cm⁻².^{1,2} The longest stability demonstrations for GDEs with over 1 000 h at 200 mA cm⁻² produce either carbon monoxide³ or formate⁴ while copper based GDEs that produce C₂+ products have a much shorter lifetime.⁵ Finally, it has been observed that faradaic current accelerates electrode failure, leading to an inverse correlation between current density and lifetime.⁶

Extensive use of GDEs in fuel cells has led to categorization of their physical and chemical failure modes.^{7,8} One of the most common failure modes is over wetting and flooding: the initially hydrophobic GDE starts to increase in hydrophilicity when faradaic current is applied, leading to water penetration which blocks gas access to the catalytic sites.^{6,9}

The shorter operational lifetimes of CO₂ electrolysis GDEs performing more complex chemistry, i.e. the production of ethylene, motivated us to hypothesize that flooding failure could be associated with the reaction products. Our experimental investigation consisted of operating Cu-based GDEs until failure and assessing the GDE surface *post-mortem* via thermolysis and characterization of outgassed species with Proton transfer reaction Time-of-flight Mass Spectrometry (PTR-TOF-MS).

GDEs consisting of Cu deposited on carbon paper (CP) were operated in a CO₂ electrolysis flow-cell at current density $J = -1.5 \text{ A cm}^{-2}$ until the onset of flooding (details in SI and in **Figures S1 and S2**). GDEs operated under N₂ flow for similar periods of time at the same current density did not flood, **Figure S3**. Water contact angle (WCA) measurements (**Figure S4**) showed that the initially hydrophobic GDE (WCA = 135°) became much more hydrophilic at the end of the run (WCA = 60°). We suspected, based on the post-run WCA, that the flooded GDE surface might

contain adsorbed hydrophilic oligomers or polymers containing oxygen, as these species typically have a WCA of 60°- 70°. ¹⁰

Identification of hydrophilic chemical species on the GDE surface is challenging, as small surface coverages can cause large changes in the WCA. Thus, rather than trying to detect the species *in situ* on the GDE, we decided to analyze the gases formed by their thermal decomposition. We found that a commercial proton-transfer time-of-flight mass spectrometer (PTR-TOF-MS) is well suited for this purpose as it has an outstanding sensitivity of 400 cps/ppbv and resolution of $m/\Delta m = 8\,000$. ¹¹

Gas phase species observed from heating as-prepared and used Cu-GDEs at 300 °C include acetaldehyde, acrolein, butene, and acetic acid (**Figure 1**). Butene is present in control samples: an as-prepared GDE and a CO-producing Ag-GDE operated at $J = -1.5\text{ A cm}^{-2}$ for 90 min (same total current passed, Figure 1b); we attribute its presence to the well-known propensity of carbon black to adsorb hydrocarbons. In contrast, acetaldehyde, acrolein, and acetic acid outgas at higher rates from the used Cu-GDE compared to the as-prepared control and the used Ag-GDE. Moreover, outgassing of acrolein increases with increasing GDE operation time, as shown in **Figure 1d** (see **Figure S5** for spectra from replicate runs of the Cu-GDEs). Clearly, the presence of these species is associated with the specific CO₂R chemistry performed by the Cu-GDE.

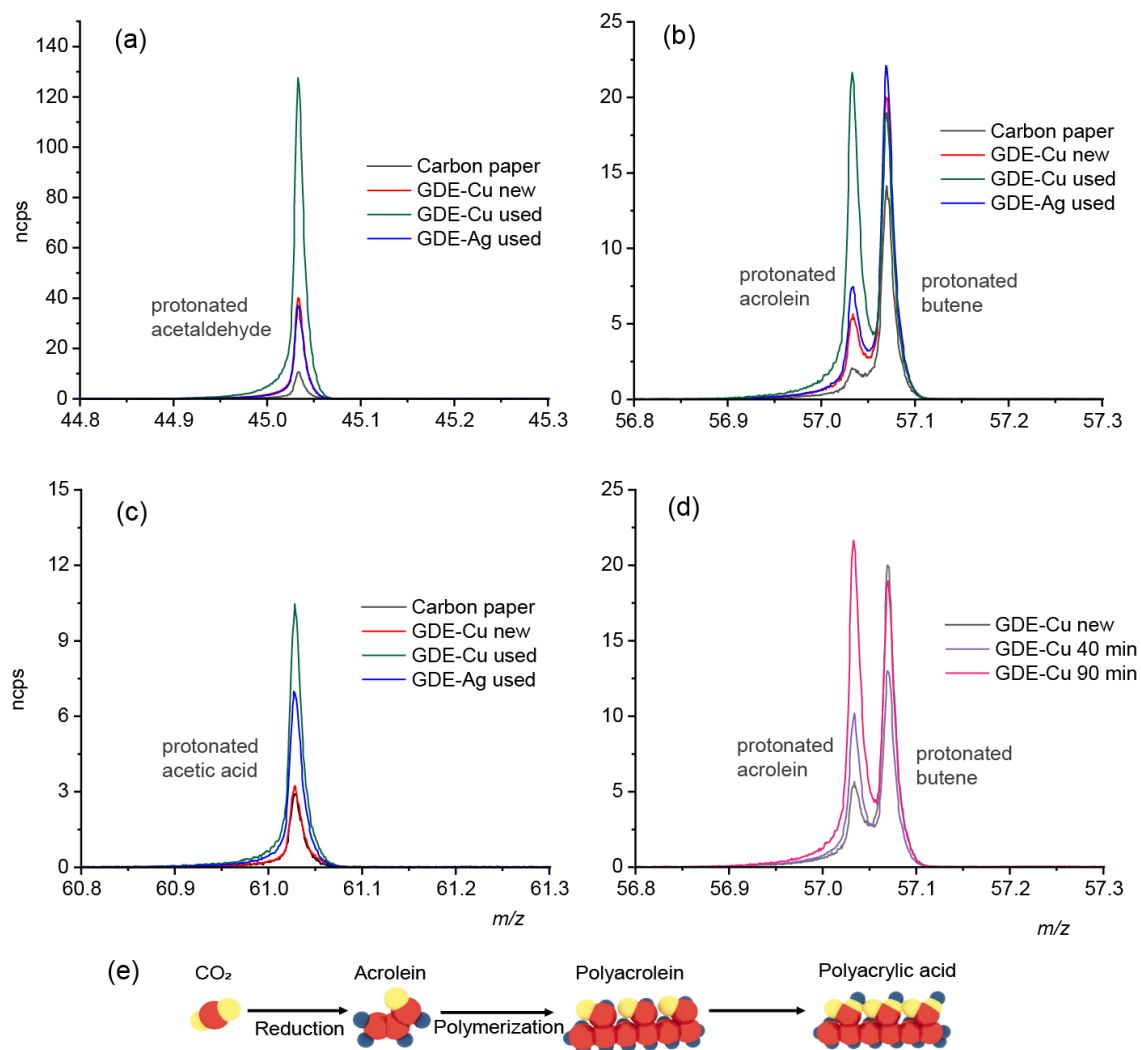


Figure 1. Time-averaged mass spectra (10 min) for species outgassing from GDEs at 300 °C: a) protonated acetaldehyde ($m/z = 45.033$); b) protonated acrolein ($m/z = 57.029$) and butene ($m/z = 57.074$); c) protonated acetic acid ($m/z = 61.028$); d) time evolution of acrolein for GDEs run for 40 and 90 min. (e) proposed mechanism for formation of polyacrylic acid via acrolein.

The prevalence of C₂-C₃ aldehydes observed in the outgassing products (**Figure S6**) during thermolysis for the used GDE suggests the formation of oligomers and polymers on the GDE surface. There are multiple oxygenated products and intermediates reported for CO₂ reduction on copper catalysts, such as acetaldehyde, propanal, acetone, formic and acetic acids, etc.¹² Formation

of these products and their corresponding intermediates has been reviewed elsewhere.¹³ However, the presence of acrolein has not been reported experimentally. We suspect that the reason it has not been detected before is its rapid polymerization under alkaline and electrochemical conditions in water, as well as poor solubility of its oligomers/polymers in water, preventing its detection by conventional analytical methods.¹⁴

The scheme shown in **Figure 1e** summarizes the proposed mechanism of formation of polyacrylic acid after exposure of the used Cu-GDEs to air. Our PTR-MS findings are consistent with previous studies of polyacrolein (PA) thermal decomposition, where the polymer starts to decompose at temperatures above 150 °C with the release of various aldehydes including acrolein itself.¹⁵ Moreover, the presence of acetic acid suggests that polyacrolein was partially oxidized into polyacrylic acid (PAA),¹⁴ which likely occurred during the time the GDE was kept on air between the end of the electrolysis run and the PTR-MS measurements.

Other evidence also suggests that PA is produced during the Cu-GDE operation. In the presence of oxygen, PAA dissolves copper nanoparticles with the formation of copper salts. This can explain the needle-like crystals containing Cu, O, and C which form after storage of the used Cu-GDEs at ambient conditions as shown in the sequence of scanning electron microscopy (SEM) images in **Figure 2**. Cracks develop in the GDE after exposing Cu to ambient air (**Figures 2a and 2b**). After storage in ambient conditions, wire-like structures (length >100 μm, diameter <1 μm) preferentially grow from the cracked surfaces (**Figures 2d-f**). Elemental imaging of the wires shows the presence of Cu, oxygen, and carbon (**Figure 2g-i**), consistent with a process of copper salt formation with polyacrylic acid (**Figure 2j**, see also additional SEM image in **Figure S7** and XRD in **Figure S8**).

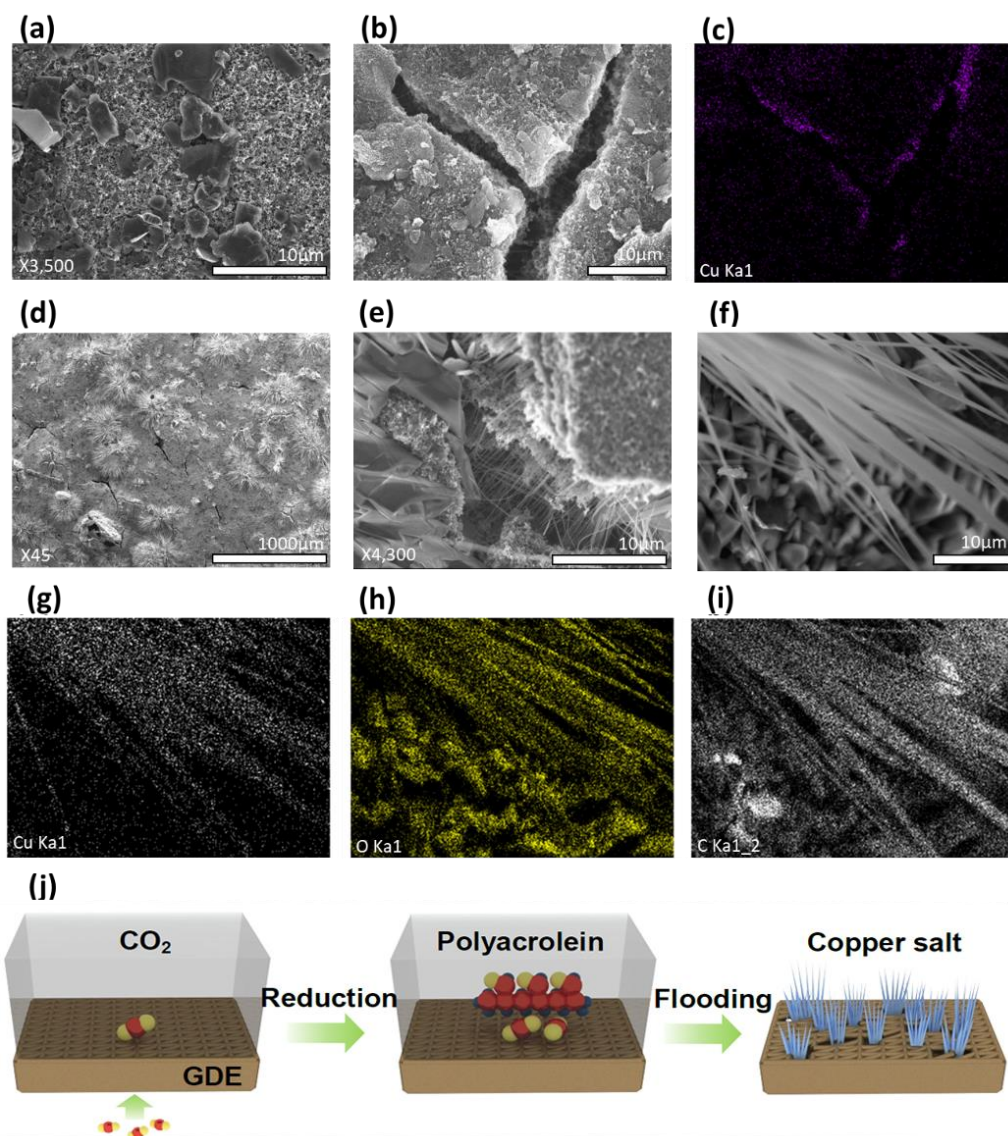


Figure 2. SEM images for (a) Fresh GDE surface; (b) GDE after use cracked surface, (c) EDX image corresponding to (b) for copper; (d) used GDE after two days at ambient conditions with needle-clusters across GDE; (e) used GDE after two days at ambient conditions magnified into crack with needle-structure; (f), used GDE after two days at ambient conditions magnified to show needle-structures; (g-i) EDX images corresponding to (f) for copper, oxygen and carbon respectively; (j) proposed mechanism for formation of Cu needles.

Data presented here shows that formation of acrolein followed by its consecutive polymerization is highly likely under the strong alkaline conditions of the electrochemical CO₂ reduction. The oligomers formed from acrolein are insoluble in the aqueous electrolyte and thus precipitate on the GDE surface. These adsorbed species have a much lower water contact angle as compared to PTFE, which allows the electrolyte to wet the GDE, eventually causing it to fail by flooding. Even prior to complete flooding, intrusion of electrolyte into the GDE reduces access of gaseous CO₂ to the catalyst; as a result, the competing hydrogen evolution reaction (HER) starts to be prevalent as shown in **Figure S2d**.

Identification of this failure mechanism for Cu-GDEs has important consequences for their application to industrial-scale CO₂ reduction. First, while the use of strongly basic electrolytes had been shown to increase FEs to useful products such as ethylene, their use may also accelerate the polymerization of minor products, reducing the useful lifetime of the system via the mechanism described here. Secondly, it points out the importance of selectivity; it would be advantageous to avoid to the degree possible the formation of reactive products such as aldehydes, although this may be difficult as they are believed to be intermediates to ethylene. Finally, it suggests that long-term operation of Cu-GDEs at industrially viable current densities in strong bases may require either maintenance or regeneration to mitigate the effects of surface hydrophilization by PA or other species.

ASSOCIATED CONTENT

Supporting Information. Methodology, Cell construction and electrolysis conditions, Flow cell characterization and products, Water contact angle, Supplemental PTR-MS data, Supplemental SEM data, Supplemental XRD data.

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Notes

The authors declare no competing financial interests.

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Investigation: GDE fabrication (MZM, HR, MKK), EC measurements (MKK, HR, MZM), PTR-MS (MKK), SEM (MKK, HCZ), WCA (MKK, MZM)

Methodology: MKK, HR

Data curation: MKK

Formal analysis: MKK, JWA

Visualization: MKK, HR, MZM, JWA

Writing – original draft: MKK, HR, MZM, JWA

Writing – review and editing: All

Supervision, Project Administration, and Funding Acquisition: JWA, AAL

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