

UNINTENDED CATION CROSSOVER IN CO₂ REDUCTION CELLS: CAUSES AND EFFECTS

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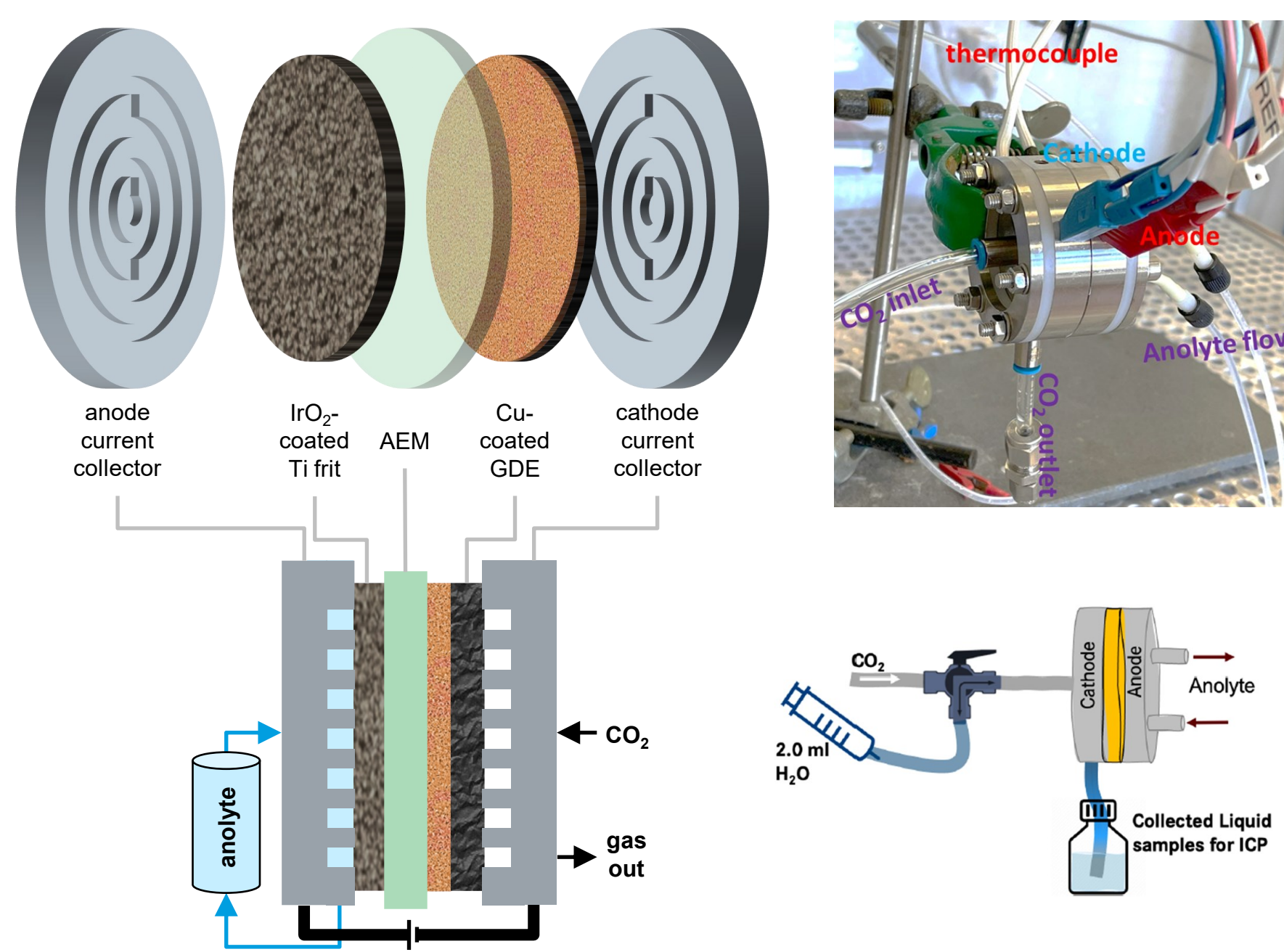
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Membrane electrode assemblies in gas diffusion cells enable CO₂ conversion at industrially relevant rates, yet their long-term operational stability is often limited by the formation of solid precipitates (e.g. K₂CO₃) in the cathode pores. This is a consequence of a combination of 1) local alkalization due to the electrochemical reaction, 2) generation of (bi)carbonate by chemical reaction of CO₂ with the alkaline electrolyte, and 3) the presence of alkali metal cations. In cath-

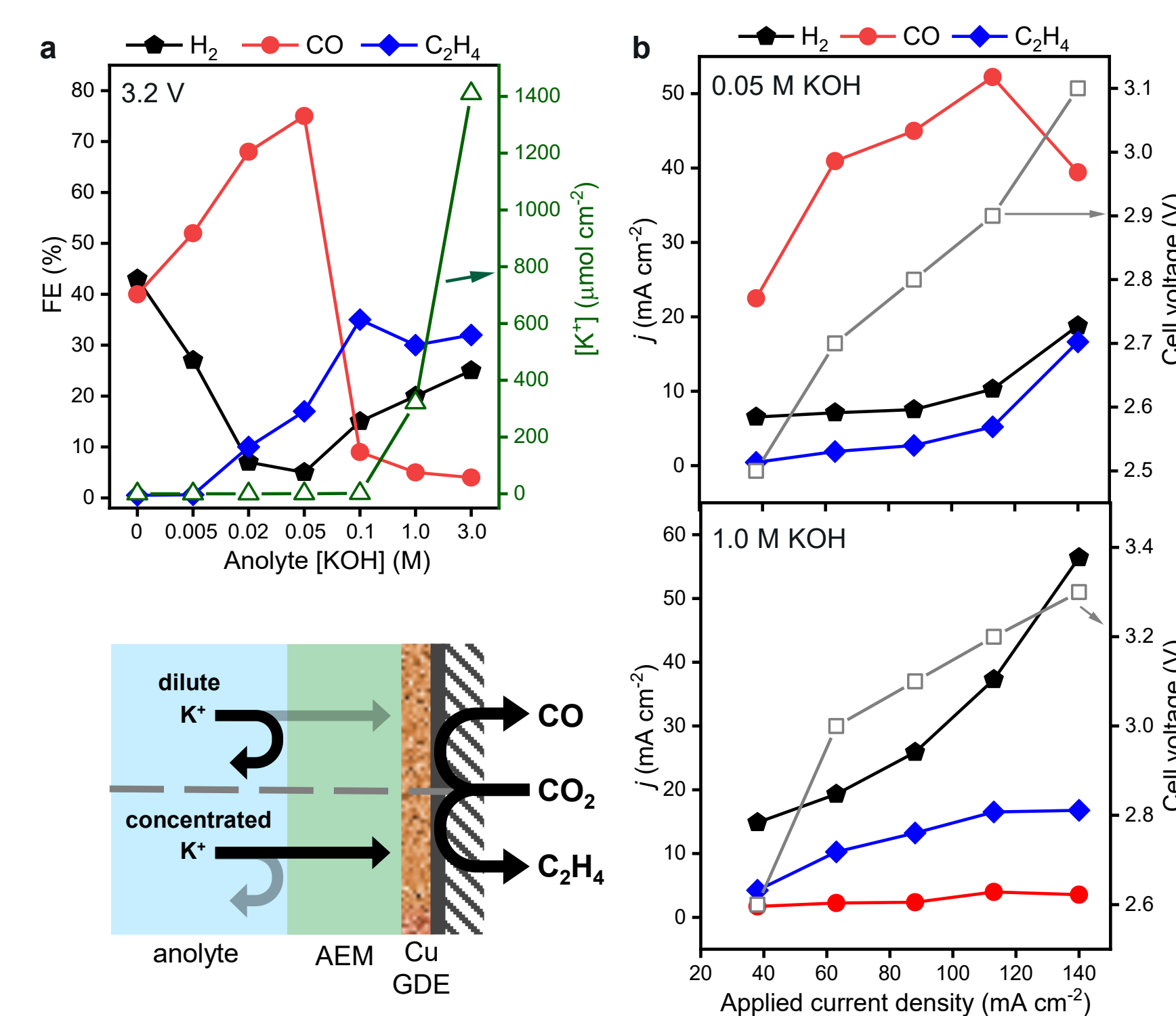
olyte-free, zero-gap cells using anion exchange membranes, the presence of electrolyte cations at the cathode is the result of unintended crossover from the anolyte, and a detailed understanding of the factors enabling this crossover is lacking. Here we show that the anolyte concentration governs the flux of cation migration through the membrane to the cathode, and this substantially influences the behaviors of copper catalysts in catholyte-free CO₂ electrolysers.

CO₂ ELECTROLYSIS IN GDE CELLS

- Zero-gap, catholyte free electrolyzer with Cu-GDE, anion exchange membrane (AEM) and recirculating anolyte (KOH).
- GDE backside is periodically flushed with aliquot of H₂O which is collected and analyzed for dissolved products.

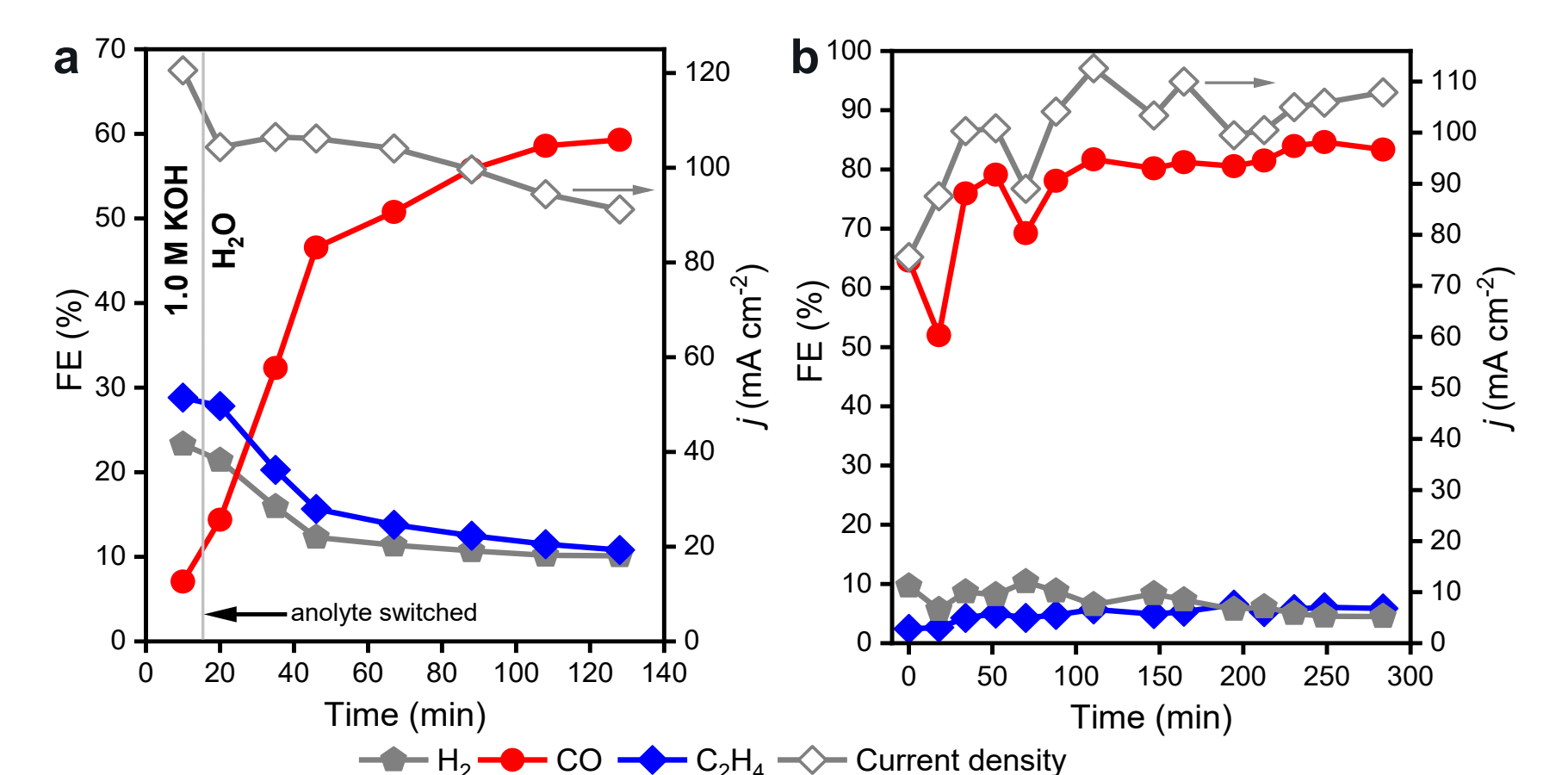


Despite the use of an AEM, cations cross from anode to cathode, correlating with drastic selectivity changes.



- Quantification of major gaseous products (FE: faradaic efficiency) and [K⁺] collected by rinsing, as a function of anolyte concentration during CO₂ electrolysis.
 - Gaseous product formation rates (as partial current densities, *j*) during constant-current operation using low and high anolyte concentrations.
- (Minor products, omitted for clarity, include acetate, methanol, ethanol, propanol)

The effects of cations appears to be reversible, and the cation-deficient operation can stably produce CO for hours.

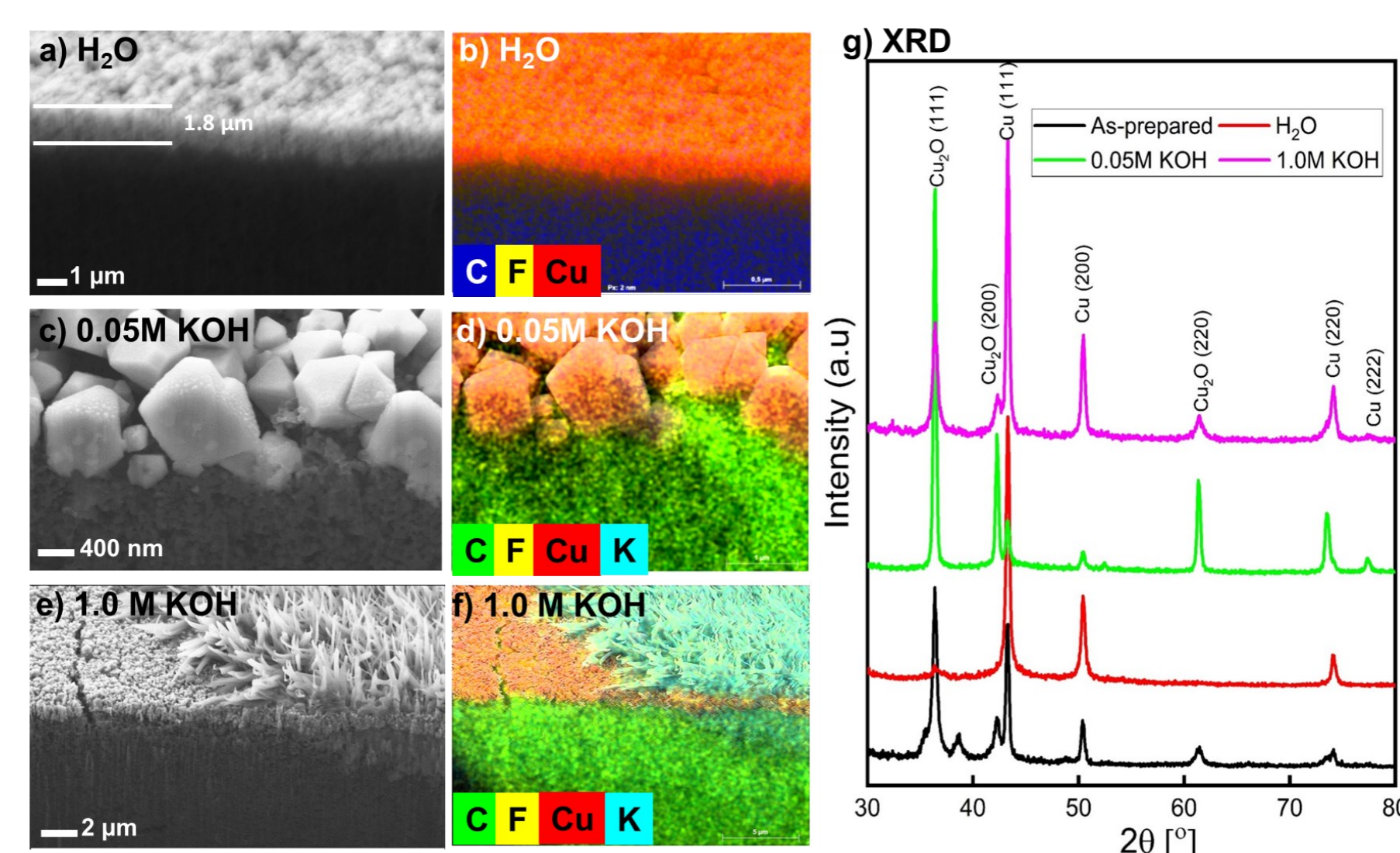


- FE and current density vs time for a device tested continuously in which the initial anolyte was 1.0 M KOH, which at 10 min was exchanged with pure water.
- FE and current density vs time for a cell with 0.05 M KOH anolyte operated continuously.

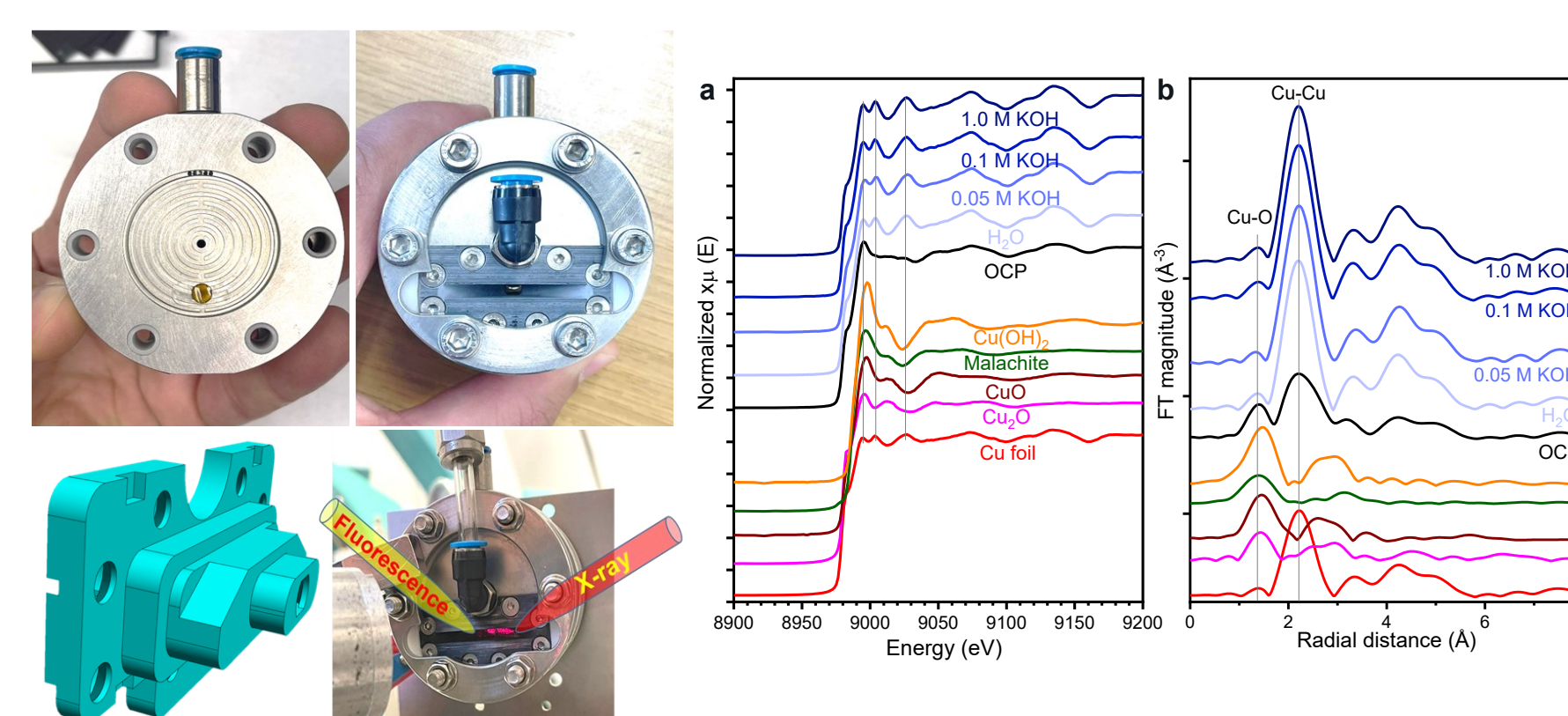
CATALYST STRUCTURE AND MORPHOLOGY

Cu speciation and morphology are sensitive to the anolyte conditions

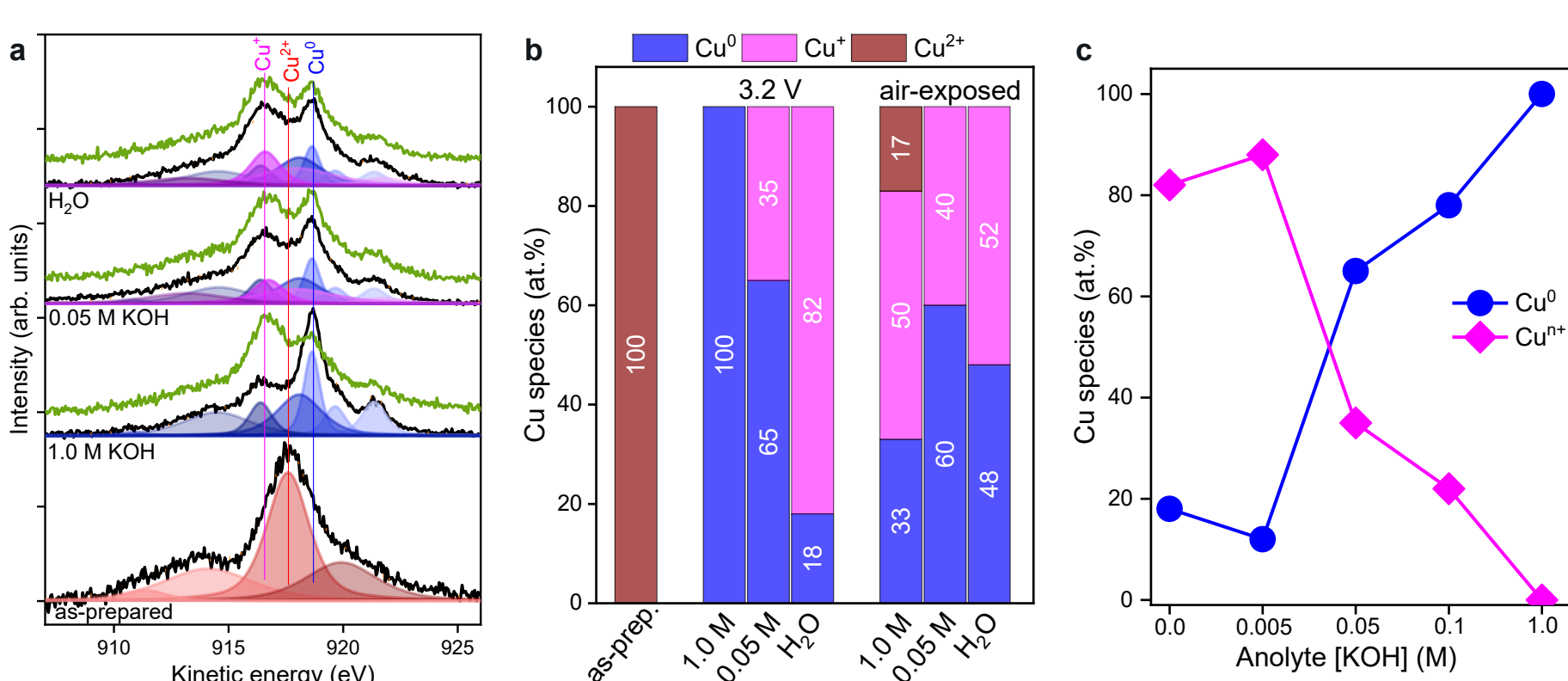
- Operando XAS (bulk sensitive) shows complete Cu reduction.
- XPS (surface sensitive) finds Cu oxidation state trends with anolyte concentration in a counter-intuitive manner, suggesting cations stabilize Cu^I whereas cation deficiency results in more oxidized Cu.
- The morphology is also affected, with Cu particle size growth under cation-deficient conditions.



SEM-EDX and XRD of Cu-GDE surface following testing under various CO₂R conditions.

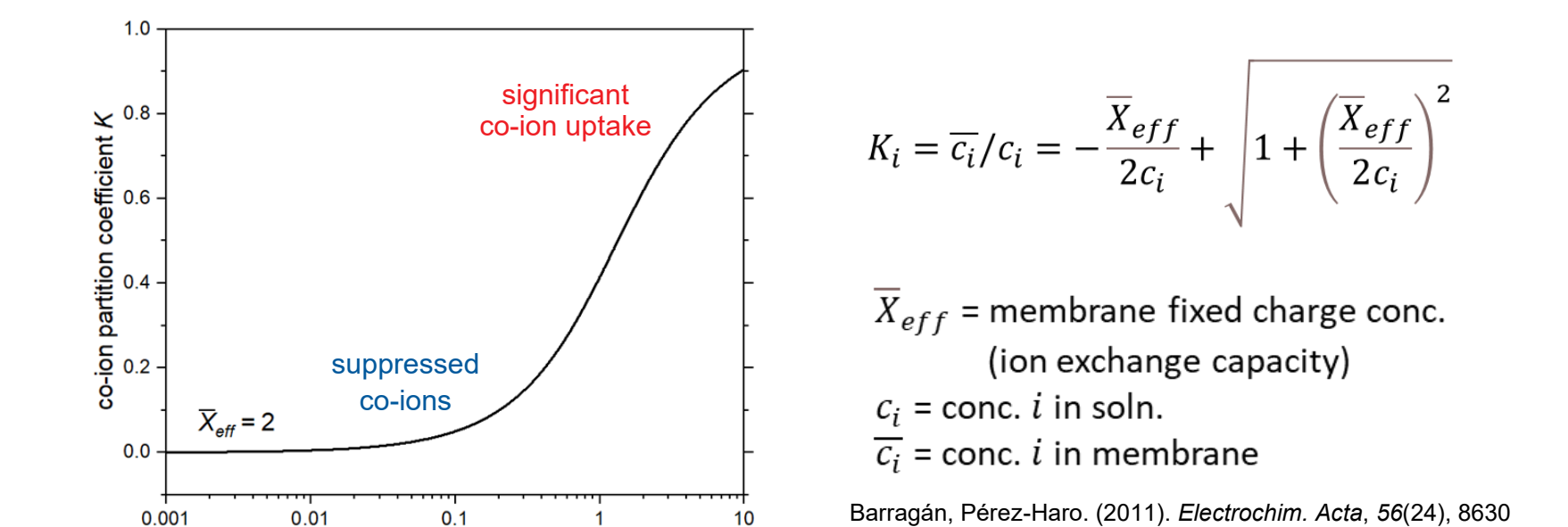


in situ X-ray absorption spectroscopy. Left) Cell photos and schematics. a) Cu K-edge XANES of cathode operated at 3.2 V using various anolyte concentrations. b) FT-EXAFS analysis, indicating characteristic Cu-O and Cu-Cu nearest neighbor distances.



Photoelectron spectroscopy following CO₂ electrolysis and air-free transfer to the analysis chamber. a) Cu Auger spectra following electrolysis under various conditions. b) Resulting quantification of Cu oxidation states. c) Speciation as function of anolyte [KOH].

AEM co-ion uptake depends on solution concentration



- Ion exchange membranes do not perfectly exclude co-ions (e.g. AEM→K⁺). An interplay between the membrane's fixed charge density and the concentration of solution ions affects the degree of co-ion uptake.
- Strong exclusion expected only when $c_i \ll X_{eff}$!
- This must be considered carefully in device design, given the strong influence of cations on CO₂R.

CONCLUSIONS

- Even in the absence of liquid catholyte, electrolyte cations play a key role in influencing CO₂ electrolysis selectivity.
- Anion exchange membranes do not perfectly exclude cations, and the degree of ion flux depends on the solution concentration and membrane properties.
- C₂ products are produced on Cu only when significant K⁺ is reaching the cathode. When cations are suppressed, CO becomes the major product.
- Cu speciation and morphology are sensitive to the anolyte condition.
- The precise mechanism by which cations influence selectivity remains to be determined. Current theories suggest alkali metal cations may influence local pH and/or surface electric fields.

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