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Effects of cation crossover through anion exchange membranes on the operation of zero-gap CO_2 electrolysers

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Gas-diffusion anion exchange membrane (AEM) electrode assemblies enable CO_2 reduction at industrially relevant rates, yet their long-term operational stability is often limited by the formation of solid precipitates in the cathode pores. This is a consequence of unintended cation crossover from the anolyte, and a detailed understanding of the factors enabling this crossover is lacking. Here we show that the anolyte concentration substantially influences the behaviors of copper catalysts in catholyte-free CO_2 electrolysers. Systematic variation of the anolyte ionic strength correlated with drastic changes in the observed product selectivity – most notably, below a threshold ionic strength, Cu catalysts produced predominantly CO, in contrast to the mixture of C_{2+} products typically observed on Cu. Operando XAS and quasi in-situ XPS were used to study how the catalyst is affected by operation conditions. Cu surface speciation was found to show a strong dependence on the anolyte concentration, wherein dilute anolytes resulted in a mixture of Cu^+ and Cu^0 surface species, while concentrated anolytes led to exclusively Cu^0 under similar testing conditions.

Methods

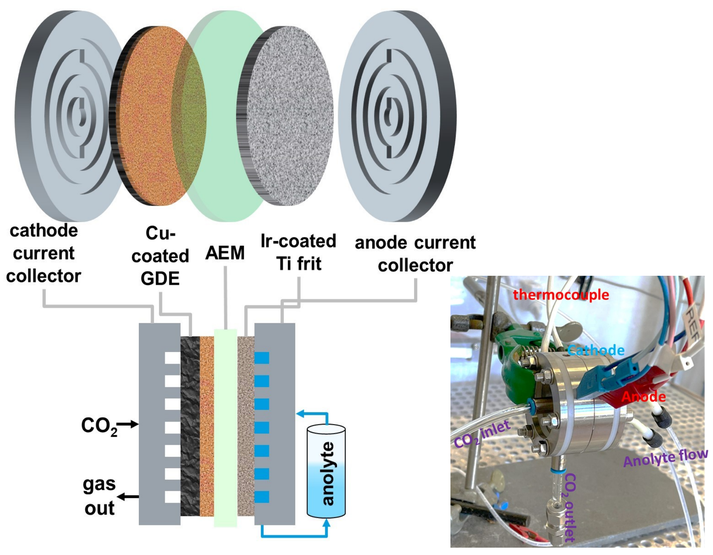


Fig.1 Schematic representation of the zero-gap electrolyser and photo of the assembled real cell and connections.

Results

- Despite AEM, K^+ reaches cathode, drastically affecting Cu CO_2R selectivity

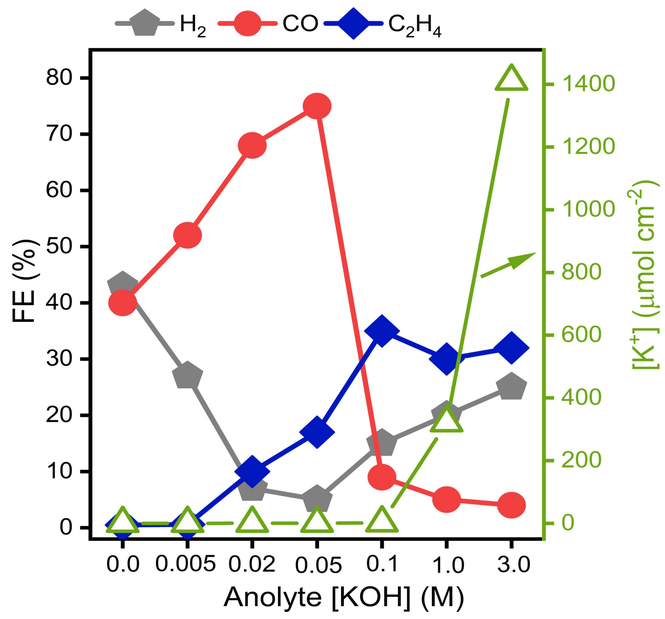


Figure 2. Faradaic efficiency (FE) distribution of the major products, and the amount of crossed-over K^+ as a function of anolyte concentration (x-axis not to scale).

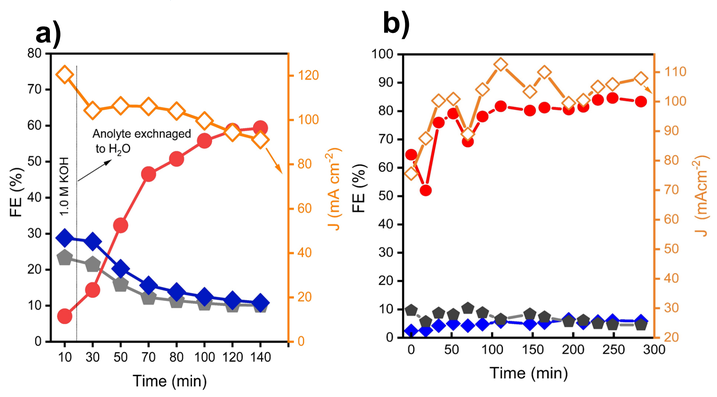


Figure 3. (a) FE and current density *vs* time for a device tested continuously in which the initial anolyte was 1.0 M KOH, which at 10 min was exchanged with pure water. (b) FE and current density *vs* time for a cell with 0.05 M KOH anolyte operated continuously.

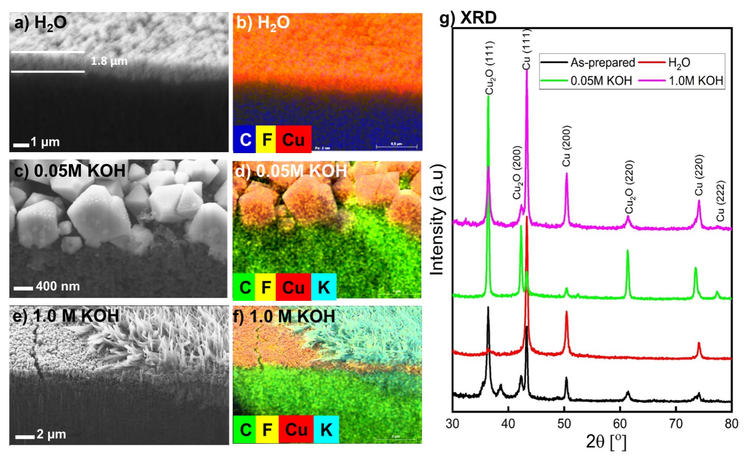


Figure 4. SEM images at FIB cross sections (a, c, e) and their respective EDX elemental mapping (b, d, f) of Cu-coated GDE cathodes after 4.5 h CO_2ER testing at 3.2 V using anolytes of H_2O, 0.05 M KOH, and 1 M KOH (respectively). g) their respective XRD patterns.

- Cathode surface speciation was found to be strongly influenced by the near surface cation concentration

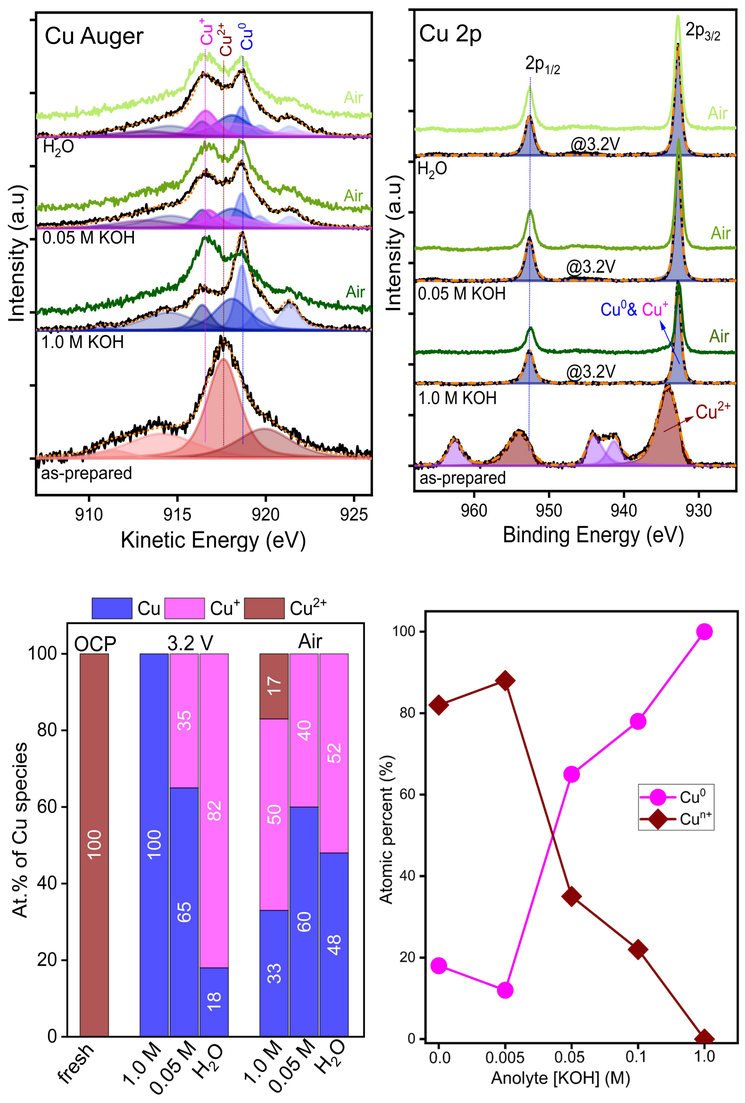
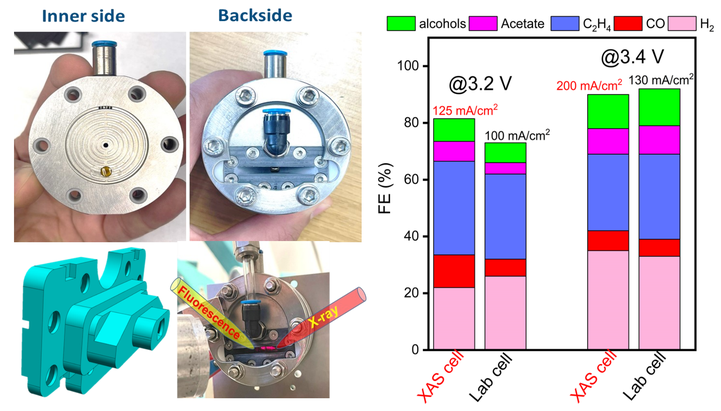


Figure 5. Quasi in situ XPS analysis of the zero-gap Cu-GDE as function of anolyte concentration.

- Amounts of crossed-over cations control the local environments near the active sites.



- Operando XAS cell replicating the lab results has been developed and validated.

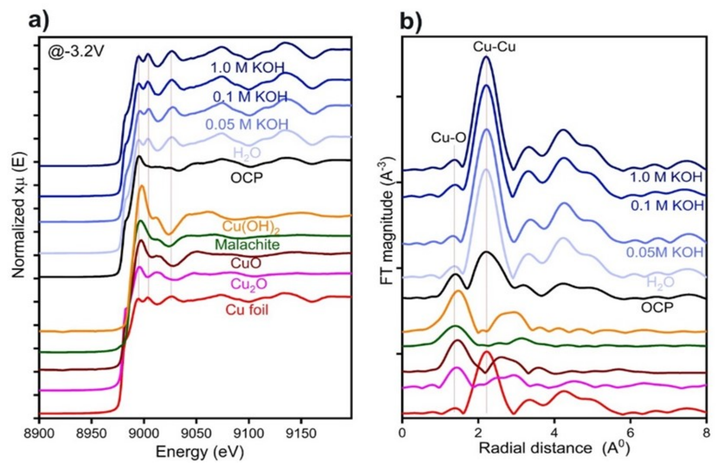
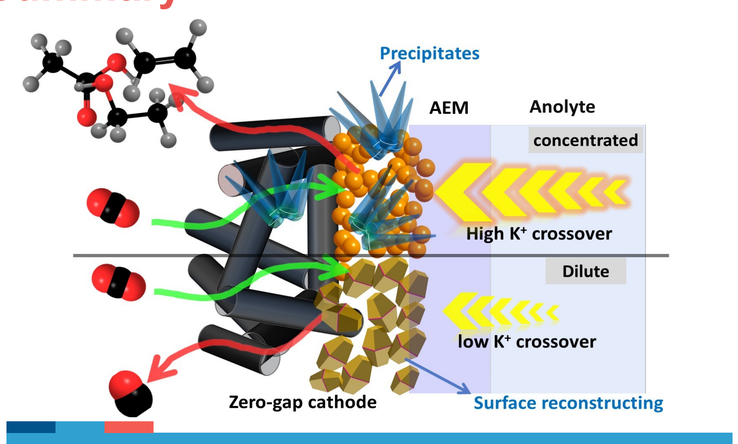


Figure 7. a) In situ Cu K-edge XANES spectra of Cu cathodes operated with H_2O and different KOH anolyte concentrations. (b) their respective k^2-weighted FT-EXAFS .

Summary



Key take-aways

- Cations have detrimental impact on the long-term operation of zero-gap electrolysers.
- Cations are essential for C-C coupling & high production rates.
- AEM excludes cations significantly at low concentrations (Donnan exclusion), but co-ion crossover occurs at high concentrations.
- Cations crossover must be considered in the future development of electrolysers and catalysts.

Acknowledgement and Partners

This work was supported in part by the Helmholtz Association's Initiative & Networking Fund (Helmholtz Young Investigators Group VH-NG-1225), and the Helmholtz Energy Materials Foundry.

The project received funding from the EU Horizon 2020 research and innovation fund under grant agreement no 862453. The materials presented and views expressed here are the responsibility of the authors only. The EU commission takes no responsibility for any use made of information set out.

The authors would like to thank eChemicles and Dr. Dirk Wallacher, HZB WI-ASE, for their contributions towards the operando cell development. We acknowledge Dr. Götz Schuck for support of in situ XAS measurement campaigns at Bessy II (KMC-2 end-station).

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European Commission | Horizon 2020 European Union funding for Research & Innovation

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