In operando NMR investigations of advanced aqueous CO_2RR systems

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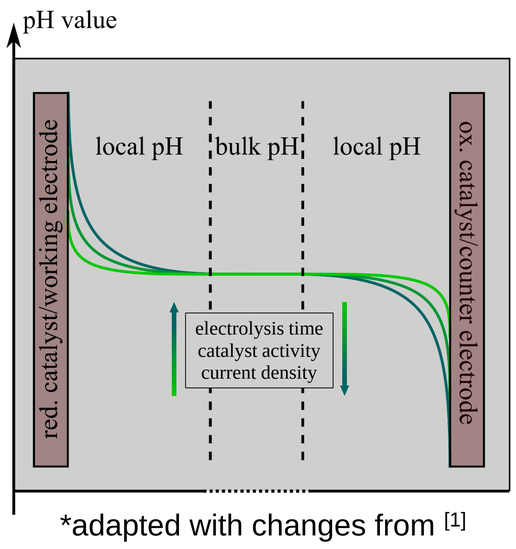
Why is local pH important?

- influences product selectivity
- determines CO_2 and H^+ availability on the WE
- may impact electrode stability



*adapted with changes from [1]

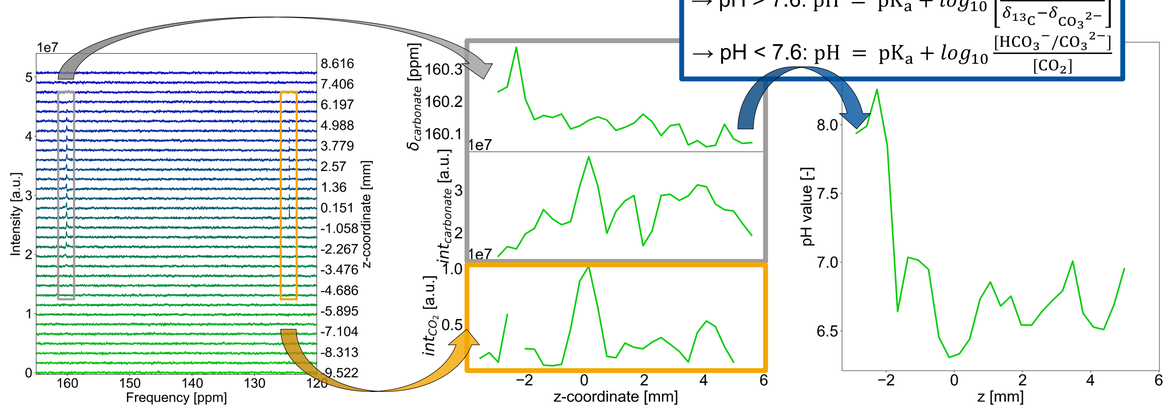
pH values from ^{13}C resonances

- pH values are determined by using the CO_3^{2-}/HCO_3^- and HCO_3^-/CO_2 equilibria depending on pH value region

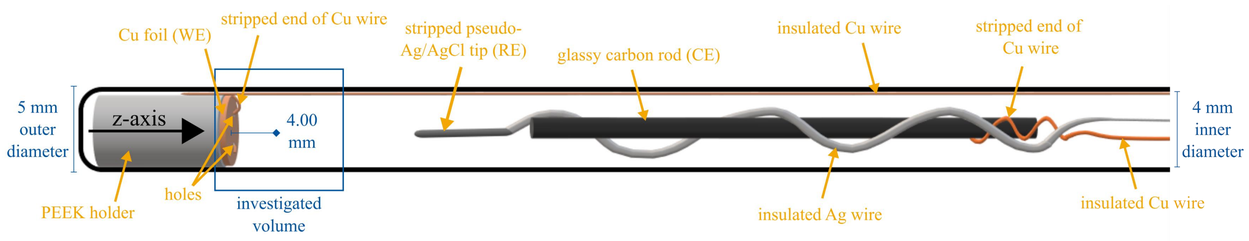
Henderson-Hasselbalch equation

→ pH > 7.6: $pH = pK_a + log_{10}\left[\frac{\delta_{^{13}C} - \delta_{HCO_3^-}}{\delta_{^{13}C} - \delta_{CO_3^{2-}}}\right]$

→ pH < 7.6: $pH = pK_a + log_{10}\frac{[HCO_3^-/CO_3^{2-}]}{[CO_2]}$

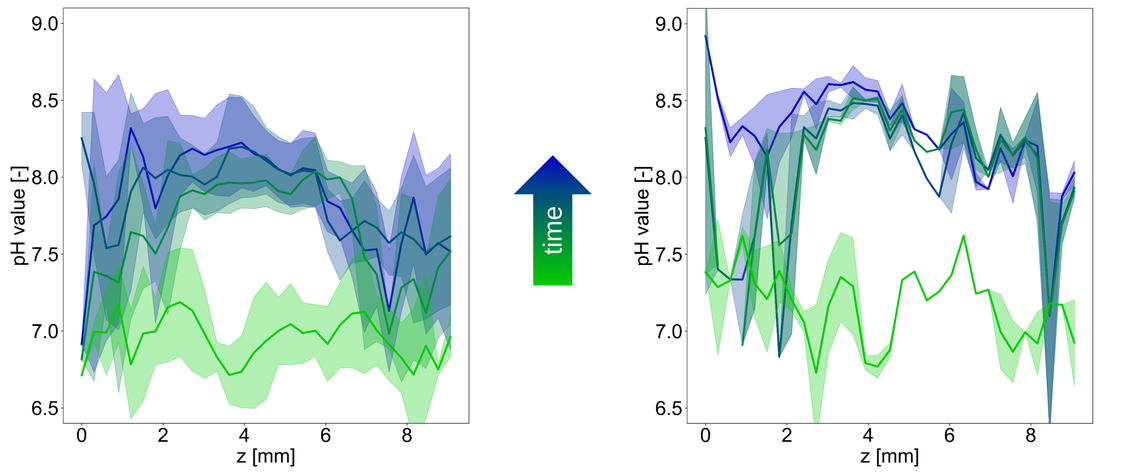


Current *in operando* NMR setup



Comparison Cu & Cu on Ag NPls

- electrolysis was conducted for 1 h in a $^{13}CO_2$-saturated 0.1 M $KH^{13}CO_3$. Averaged over (i) 3 and (ii) 2 experiments.



Cu foil as WE, d = 4 mm

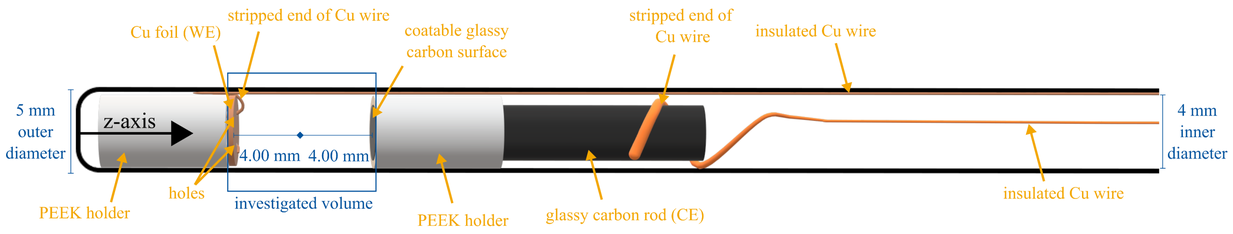
Cu on Ag NPls[2] as WE, d = 4 mm

- local pH values are slightly higher for the novel catalyst

Outlook

- local pH evolution will be compared to Ag foil to correlate Cu content and pH values
- investigation of various selected cell potentials to evaluate the impact of electrochemical potential on local pH

Advanced setup for pH near CE

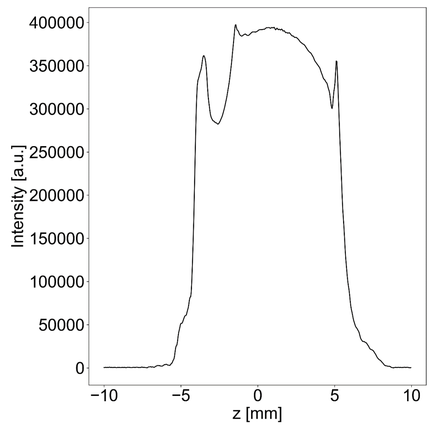


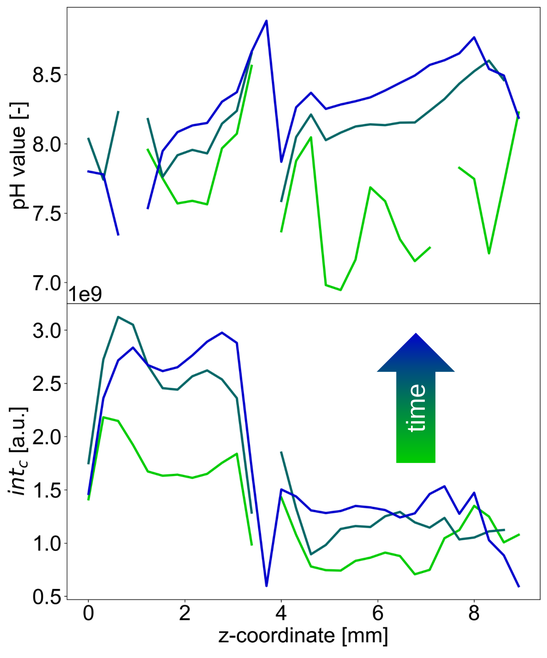
Outlook

- optimization of cell setup to prevent bubble distortions
- application of Ni-Co-O ink to the GC CE (d = 2 or 3 mm)
- influence of OER-optimized catalyst and electrolyte on the CO_2RR as well as effect of local pH on catalyst stability

First tests

- pH value increases at both electrodes, but why?
- bubble distortions identified by HCO_3^-/CO_3^{2-} integral and ^1H image





[1] A. S. Varela, Current Opinion in Green and Sustainable Chemistry 2020, 26, 100371.

[2] E. Robens, B. Hecker, H. Kungl, H. Tempel, R.-A. Eichel, ACS Appl. Energy Mater. 2023, 6, 7571.