Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Modeling Gas Diffusion Electrodes for CO_2 Reduction Supplementary Information

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Catalyst layer saturation curve and equivalent electrolyte film thickness

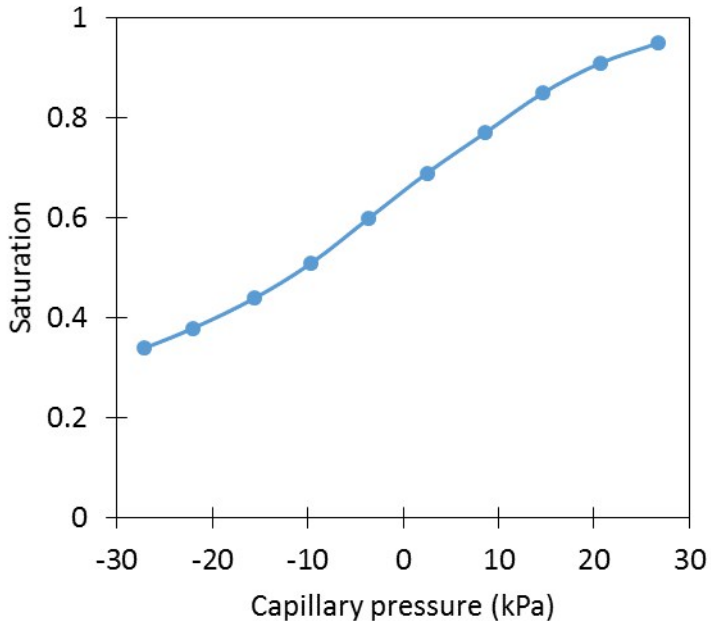

Figure S1 Saturation vs capillary pressure relationship for the catalyst layer.[1]

The equivalent electrolyte thin film thickness, $\delta_{TF,eq}$ is derived geometrically from the Saturation, assuming cylindrical CL pores with pore radius $r_{p,CL}$

$$\frac{\pi\left(r_{p,CL}-\delta_{TF,eq}\right)^2}{\pi r_{p,CL}^2}=1-S\#(S1)$$

which can be simplified to equation (1).

Extracting kinetic parameters from planar electrode experiments

A one-dimensional model is constructed to correct for mass transport effects in the planar electrode experiments performed by Hatsukade et al.[2] A boundary layer (BL) of 140 µm is assumed. Species flux is calculated using Nernst-Planck's equation, assuming no convection within the boundary layer. Bicarbonate acid/base reactions and water dissociation reactions are accounted for. Species concentration is set to that of 0.1 M $KHCO_3$ saturated with 1 atm CO_2 at the bulk/BL boundary, assuming well-mixed condition. CO_2 and OH^- flux is set to experimentally measured values at the BL/electrode boundary, and zero flux for all other species. This allows us to determine local species concentration at each total current density condition, shown in Figure S2. The local concentration is then used to fit concentration dependent Tafel equations, equations (27) and (28), assumed for COER and HER to extract the exchange current densities and charge transfer coefficients.

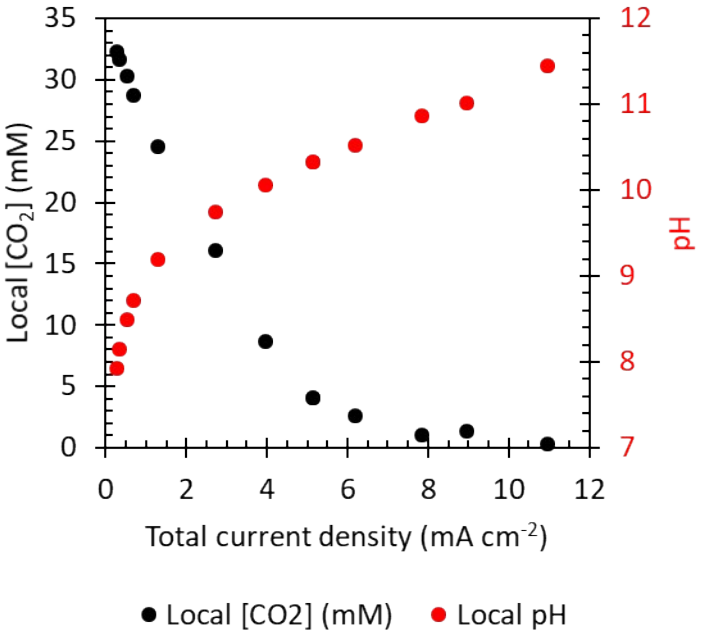

Figure S2 Local CO_2 concentration and local pH calculated as a function of total current density.

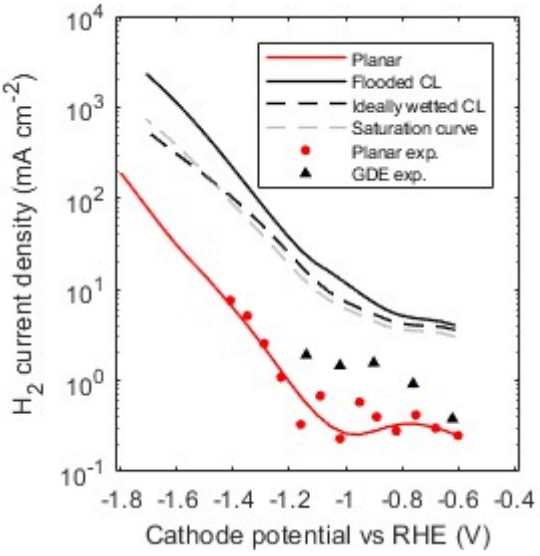

Figure S3 H_2 partial current density as a function of Cathode potential vs RHE for the planar case, flooded case, ideally wetted case, saturation curve case, compared to experimental data measured by Hatsukade et al. and Verma et al

Partial H2 current density

Effects of catalyst layer wettability

H_2 current density is not affected by the CL saturation (Figure 7a) as shown in Figure S4. H_2 local current density remains fairly constant throughout the CL since its rate is independent of the concentrations of dissolved gaseous species.

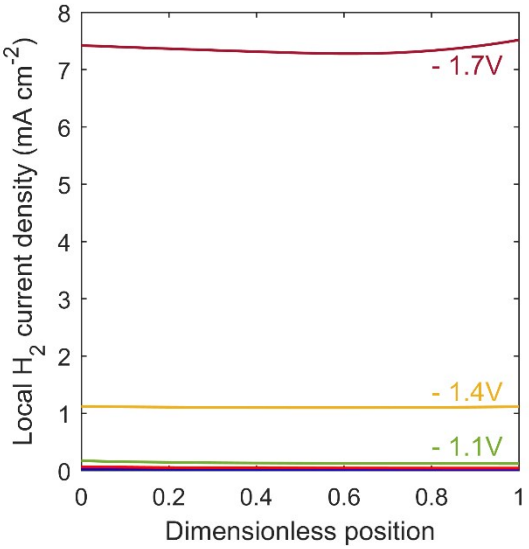

Figure S4 Local H_2 current density as a function of dimensionless position within the CL.

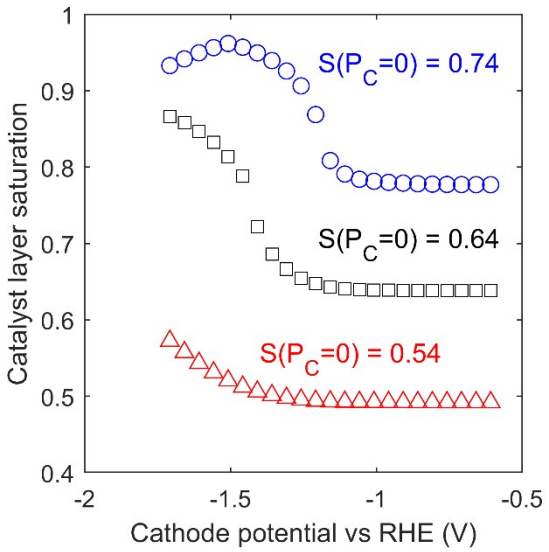

Figure S5 CL average saturation as a function of cathode potential for a more hydrophilic CL (blue circles) and more hydrophobic CL (orange triangles) compared to the base case (grey squares).

The average CL saturation is shown in Figure S5. CL saturation remains near zero capillary pressure saturation (S = 0.64) for potentials less cathodic than -1.1 V vs RHE, indicating that the "ideally wetted case" is a good approximation for this potential region. The more hydrophilic CL reaches 0.9 saturation at -1.3 V vs RHE, causing the decrease in CO current density shown in Figure 8.

1. I. V. Zenyuk, P. K. Das and A. Z. Weber, *J. Electrochem. Soc.*, 2016, **163**, F691-F703.
2. T. Hatsukade, K. P. Kuhl, E. R. Cave, D. N. Abram and T. F. Jaramillo, *Phys. Chem. Chem. Phys.*, 2014, **16**, 13814-13819.