## Supplemental Information

## Title:

# In-Depth Understanding of the $CO_2$ Limitation of Air Fed Anion Exchange Membrane Fuel Cells

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**Water uptake:**

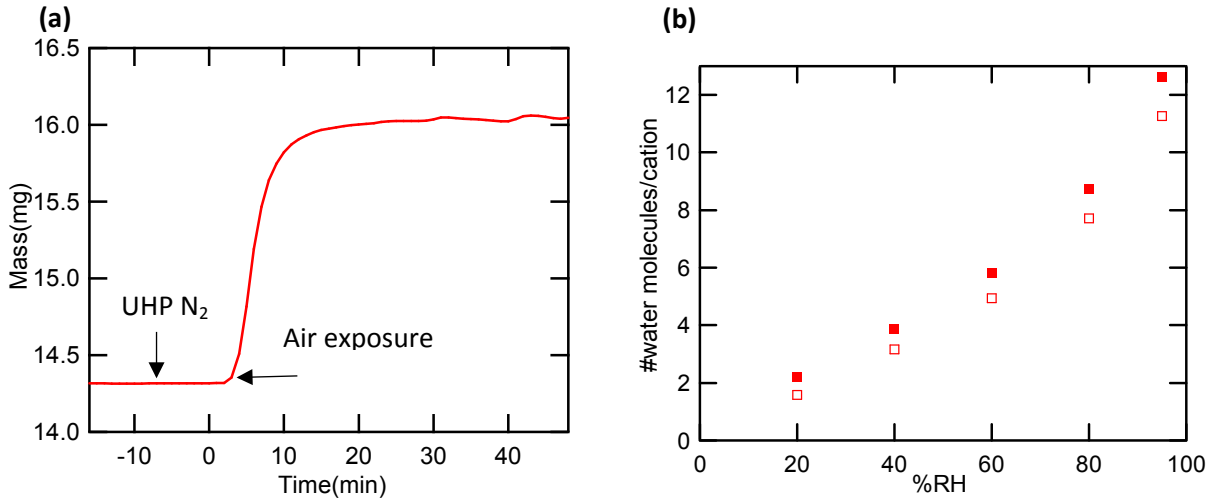



Figure. S1: (a) Mass uptake for the membrane when it is exposed to ambient air at 60 °C and 85%RH containing 400 ppm $CO_2$.(b) No. of water molecules per cation(λ) vs %RH for Pure $OH^-$ (closed squares),[1] and $HCO_3^-$ form exposed to $CO_2$ free $N_2$ gas for 24 h (60 °C & 75%RH) before testing the water content.

**Small-angle x-ray scattering:**

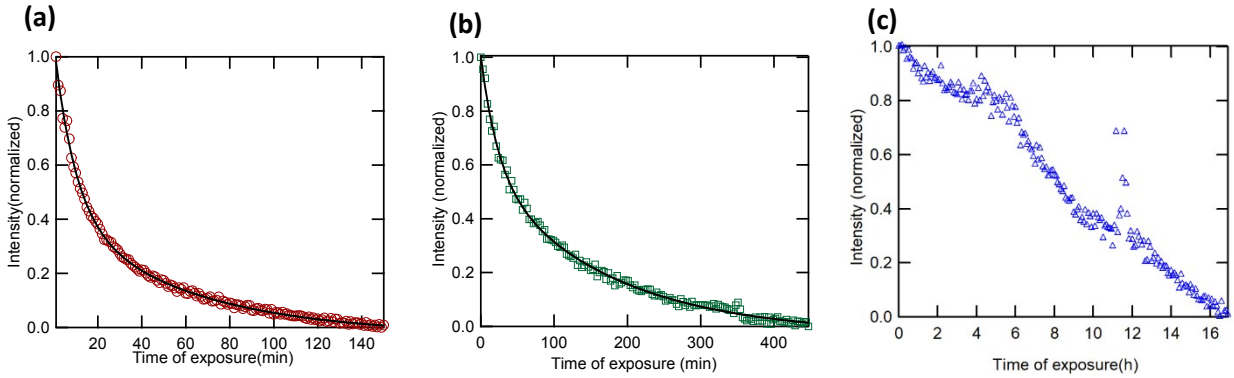



Figure. S2: Transient drop in intensity of the ionomer feature, q ~ 0.12 to 0.15 $Å^{-1}$, for the membrane vs time at (a) 50%RH, (b) 75%RH and (c) 85%RH when exposed to air containing 400 ppm $CO_2$.

**Wide-angle x-ray scattering:**

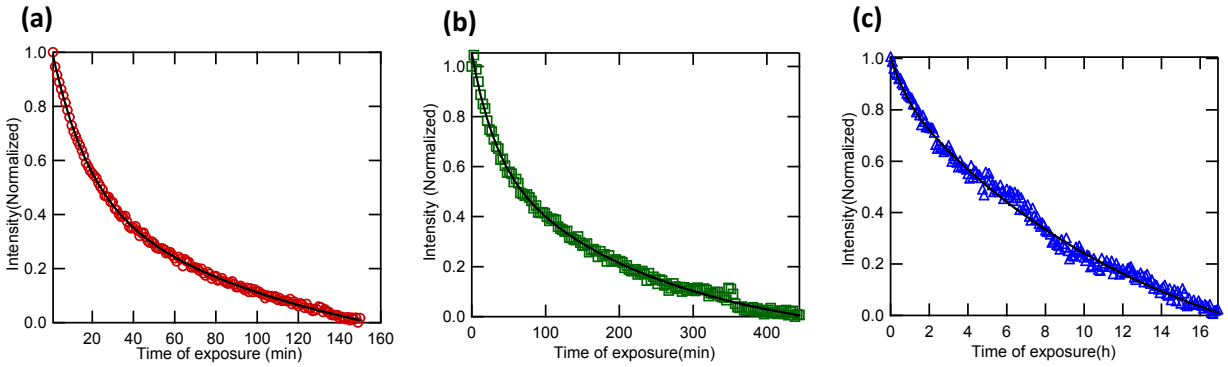



Figure. S3: Transient drop in the intensity of the interchain $CF_2$-$CF_2$ spacing feature, q =1.2 $Å^{-1}$, for the membrane vs time at (a) 50%RH, (b) 75%RH and (c) 85%RH when exposed to air containing 400 ppm $CO_2$.

**WAXS Area of feature vs time**

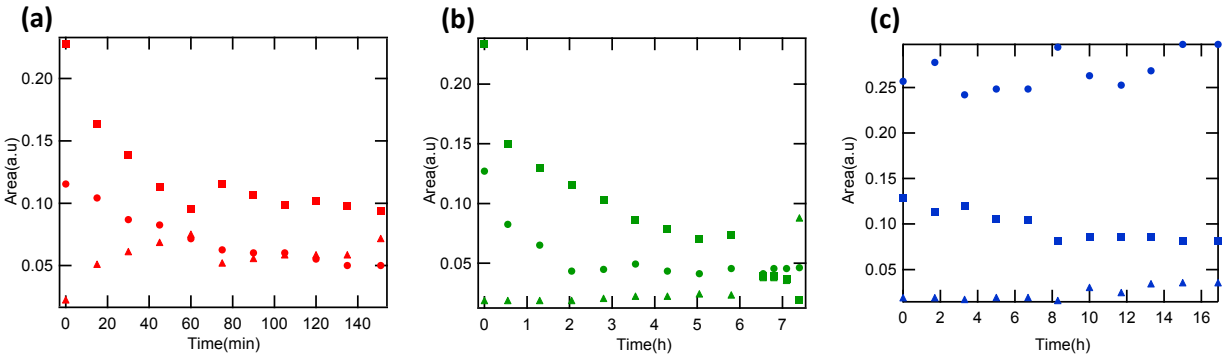



Figure. S4: Transient drop in the area of the gaussian features fit to the wide-angle x-ray scattering data for the membrane observed at q=1.1 $Å^{-1}$(circles), q=1.2 $Å^{-1}$ (squares) and q=1.5 $Å^{-1}$ (triangles) at (a) 50%, (b) 75% and (c)85%RH when exposed to air containing 400 ppm $CO_2$.

The detailed analysis of Gaussian change in height(intensity), width:

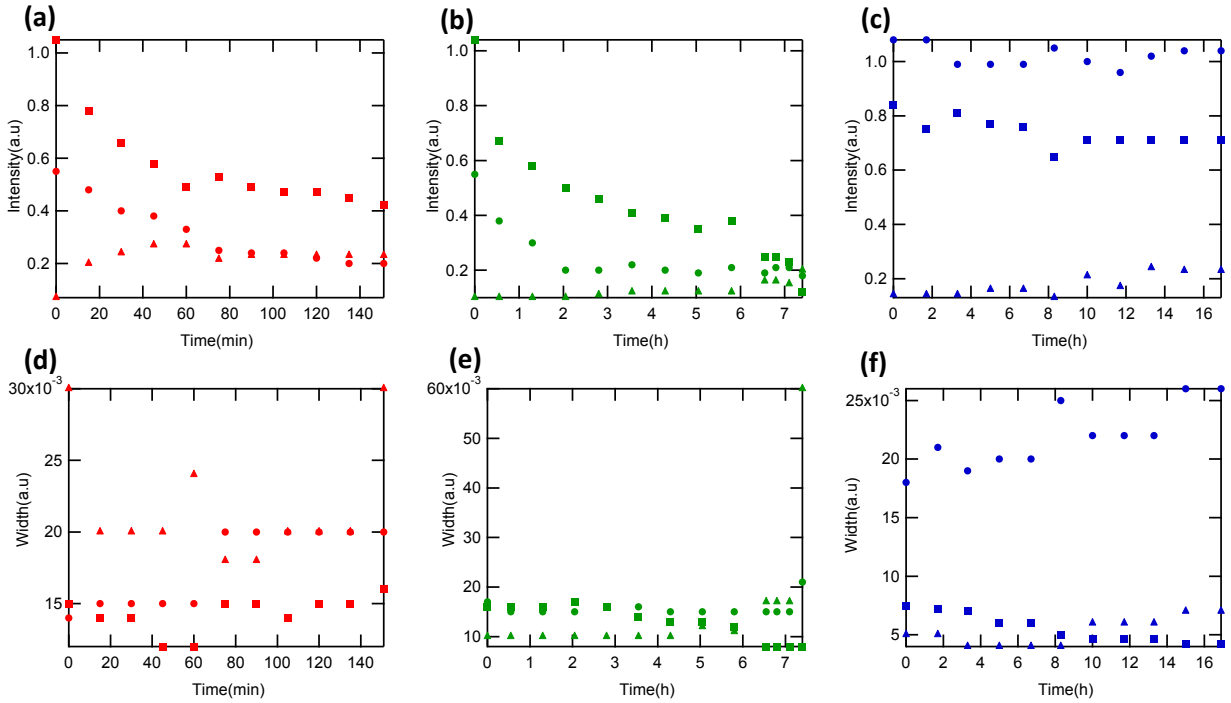
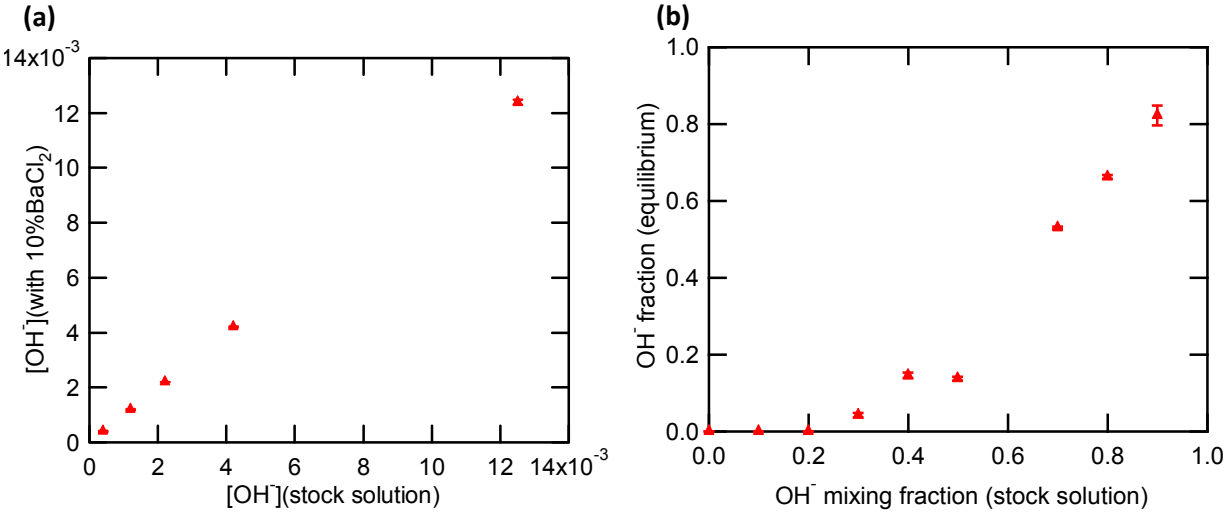



Figure. S5: Transient change in the height (intensity) of the gaussian peaks, q =1.1, 1.2 & 1.5 $Å^{-1}$ fit to the wide-angle x-ray scattering data for the membrane, at (a) 50 %RH, (b) 75%RH and (c) 85%RH when exposed to air containing 400 ppm $CO_2$. Transient change of the width of the gaussian peaks, q =1.1, 1.2 & 1.5 $Å^{-1}$ fit to the wide-angle x-ray scattering data for the membrane at (d) 50%RH, (e) 75%RH and (f) 85%RH when exposed to air containing 400 ppm $CO_2$.

**Titration:**



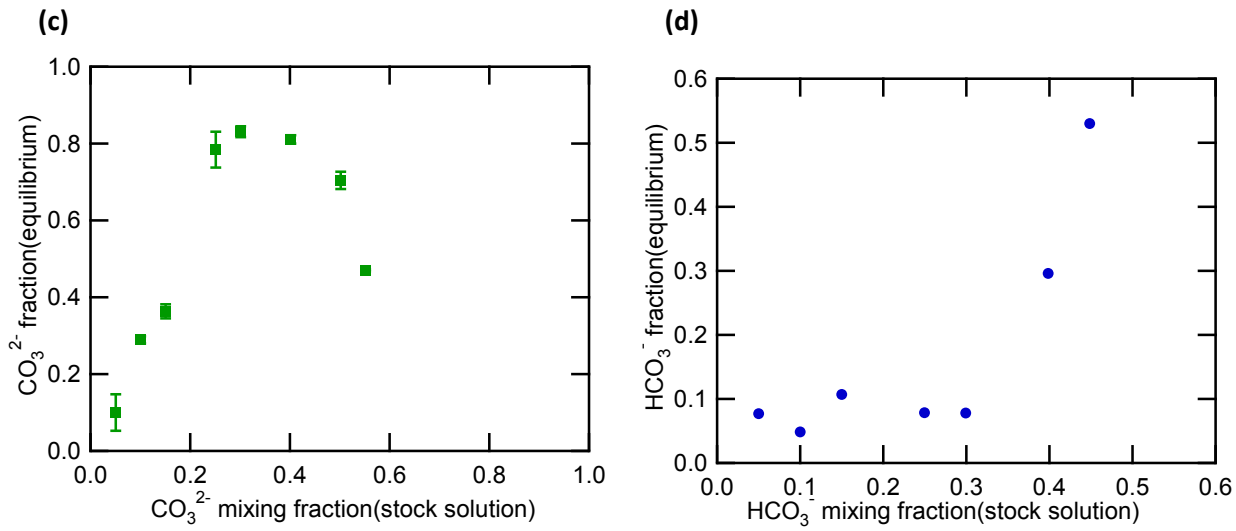



Figure. S6: Ionic equilibrium of stock solution titration mixtures. (a) Data for titration of stock solution containing only $OH^-$ ions (with 10% excess $BaCl_2$ solution) vs titration of stock solutions containing only $OH^-$ ions without $BaCl_2$. Equilibrium fraction of (b) $OH^-$, (c) $CO_3^{2-}$, (d) $HCO_3^-$ ions as evaluated from the titrations vs the mixing fraction of $OH^-$, $CO_3^{2-}$ and $HCO_3^-$ ions in the stock solution.

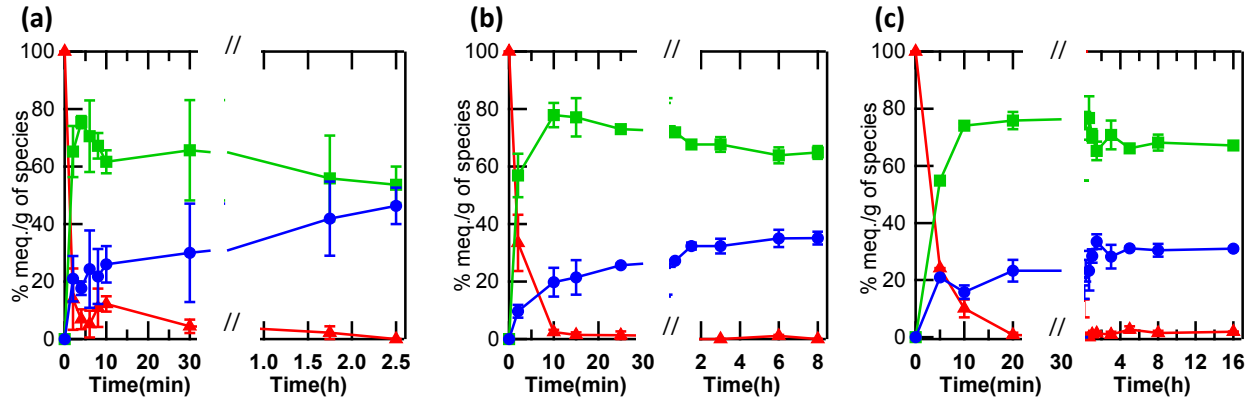



Figure. S7: Species concentration profile of $OH^-$(red triangle), $CO_3^{2-}$(green square) and $HCO_3^-$(blue circle) in the membrane vs time of exposure to air containing 400 ppm $CO_2$ at 60 °C and (a)50%, (b)75% and (c)85%RH. *Note: The figure is included for interest. Although the three species exist qualitatively the absolute values are not reliable to make a quantitative conclusion about the kinetics of $CO_2$ reaction.*

Fuel cell data supplementary information:

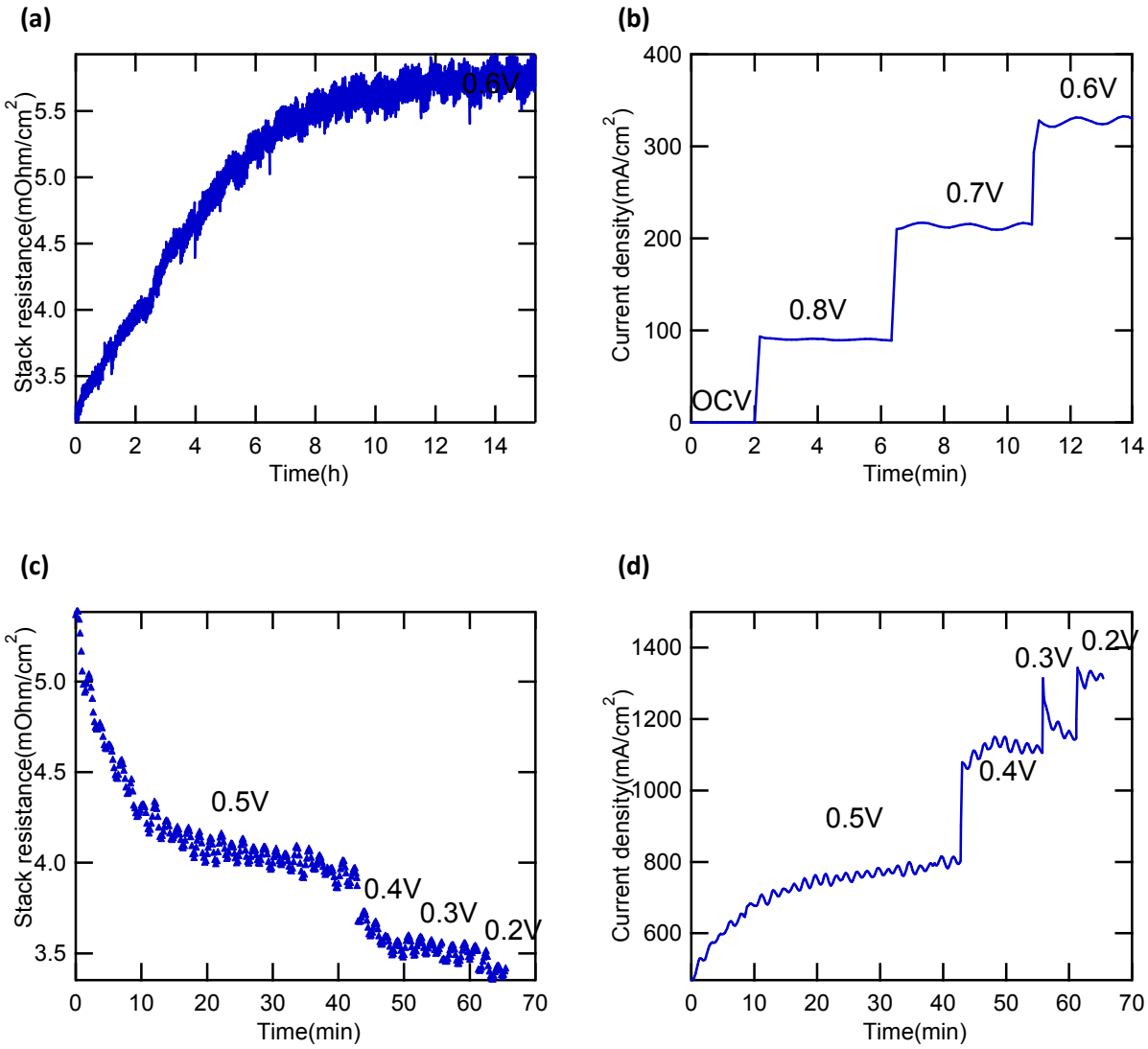



Figure. S8: Fuel cell data of PFAEM ionomer and membrane with Pt/C loading of 0.485 mg/cm$^2$, on each electrode, operated at 60 °C using $H_2$/ Ambient air (400 ppm $CO_2$) and 85%/85%RH at anode/cathode. [a] Stack resistance vs time when the fuel cell is switched from clean air to ambient air (400 ppm $CO_2$) [b]. Current density vs time when a fully air equilibrated fuel cell operated at voltages between OCV and 0.6V. [c]. Stack resistance vs time when a fully air equilibrated fuel cell is operated at voltages between 0.5V and 0.2V. [d]. Current density vs time when a fully air equilibrated fuel cell is operated at voltages between 0.5V and 0.2V.

**References:**

1. A. G. Divekar, A. M. Park, Z. R. Owczarczyk, S. Seifert, B. S. Pivovar and A. M. Herring, *ECS Transactions*, 2017, **80**, 1005-1011.