Supplemental Information

Title:

In-Depth Understanding of the CO$_2$ Limitation of Air Fed Anion Exchange Membrane Fuel Cells

Authors:

Ashutosh G. Divekar,$^a$ Ami C. Yang-Neyerlin,$^b$ Christopher M. Antunes,$^b$ Derek J. Strasser,$^b$ Andrew R. Motz,$^a$ Soenke S. Seifert,$^c$ Xiaobing Zuo,$^c$ Bryan S. Pivovar,$^b$ and Andrew M. Herring$^a$*

Affiliations:

$^a$ Colorado School of Mines

$^b$ National Renewable Energy Laboratory

$^c$ Advanced Photon Source, Argonne National Laboratory

**Corresponding author:** Prof. Andrew Herring (aherring@mines.edu)†
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 CO₂. (b) No. of water molecules per cation(λ) vs %RH for Pure OH⁻ (closed squares),¹ and HCO₃⁻ form exposed to CO₂ free N₂ 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 CO₂.
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:

![Graphs showing transient change in height and width of Gaussian peaks.](image)

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 CO₂.

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 CO₂.

Titration:

![Graph showing titration results.](image)
Figure. S6: Ionic equilibrium of stock solution titration mixtures. (a) Data for titration of stock solution containing only OH⁻ ions (with 10% excess BaCl₂ solution) vs titration of stock solutions containing only OH⁻ ions without BaCl₂. Equilibrium fraction of (b) OH⁻, (c) CO₃²⁻, (d) HCO₃⁻ ions as evaluated from the titrations vs the mixing fraction of OH⁻, CO₃²⁻ and HCO₃⁻ ions in the stock solution.

Figure. S7: Species concentration profile of OH⁻ (red triangle), CO₃²⁻ (green square) and HCO₃⁻ (blue circle) in the membrane vs time of exposure to air containing 400 ppm CO₂ 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 CO₂ reaction.
Fuel cell data supplementary information:

(a) Stack resistance vs time when the fuel cell is switched from clean air to ambient air (400 ppm CO₂) [a]. Current density vs time when a fully air equilibrated fuel cell operated at voltages between OCV and 0.6V. [b]. Stack resistance vs time when a fully air equilibrated fuel cell is operated at voltages between 0.5V and 0.2V. [c]. Current density vs time when a fully air equilibrated fuel cell is operated at voltages between 0.5V and 0.2V.

Figure. S8: Fuel cell data of PFAEM ionomer and membrane with Pt/C loading of 0.485 mg/cm², on each electrode, operated at 60 °C using H₂/Ambient air (400 ppm CO₂) 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 CO₂) [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: