



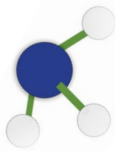
Simulation-based Sensitivity Analysis Of The Direct Ammonia Fuel Cell Operating Conditions

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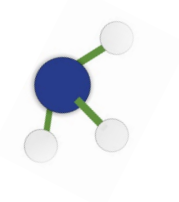
Comsol conference, München



Outline



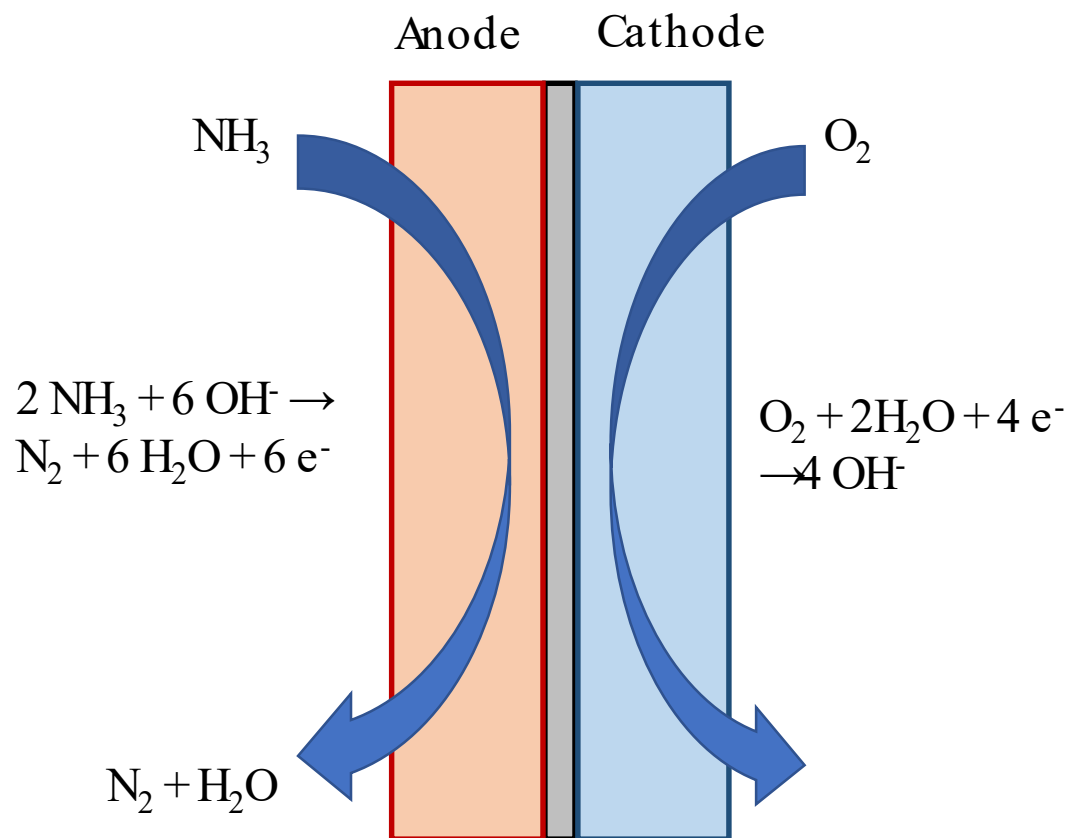
1. Direct ammonia fuel cell operation and model in general
2. Model details and validation
3. Sensitivity to operating conditions, importance of different loss components



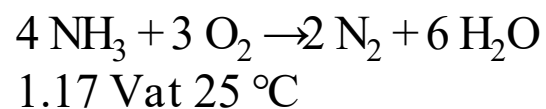
Direct Ammonia Fuel Cell and Model

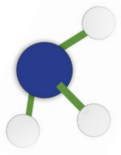


Direct Ammonia Fuel Cell

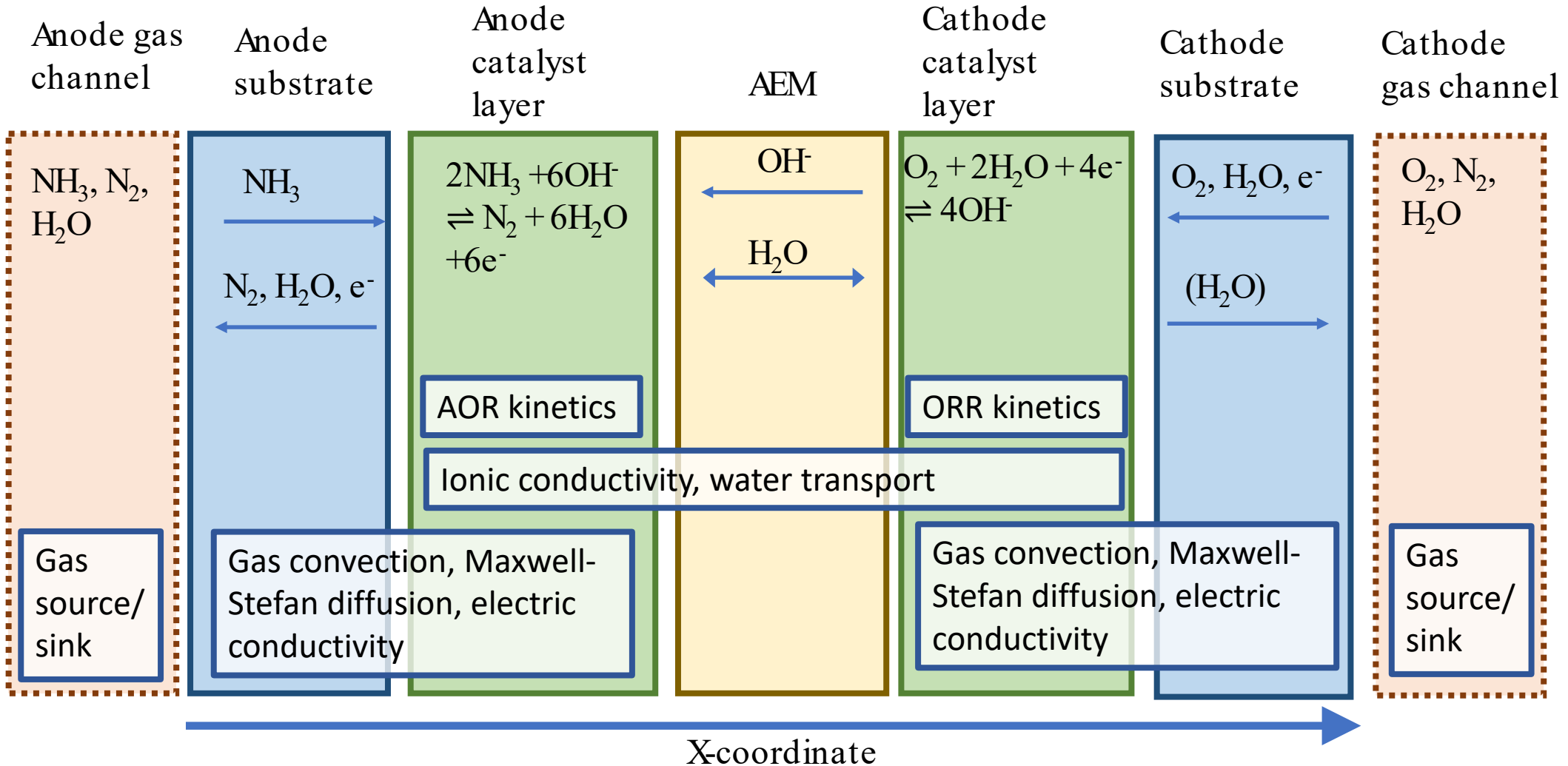


- Fuel cell that uses ammonia directly as a fuel.
- Theoretical voltage at room temperature 1.17 V.
- Ammonia can be liquefied at a lower pressure than H_2 .
- Considered especially for heavy-duty transport.
- No CO_2 emissions.
- Slow kinetics of the ammonia oxidation reaction (AOR) at anode are the main voltage loss component





DAFC Comsol Model in General

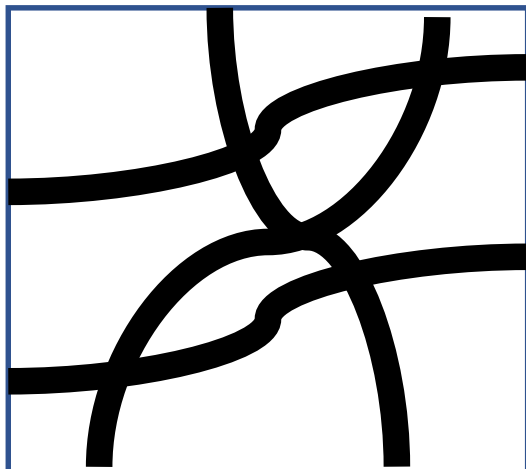




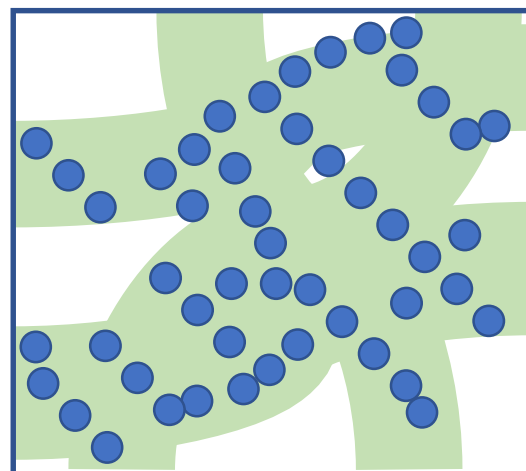
Electrode Structures



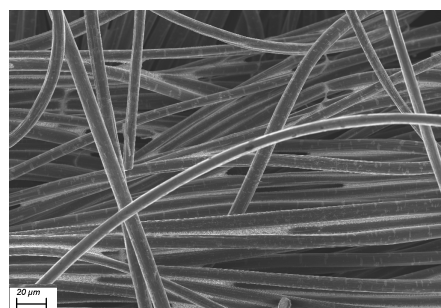
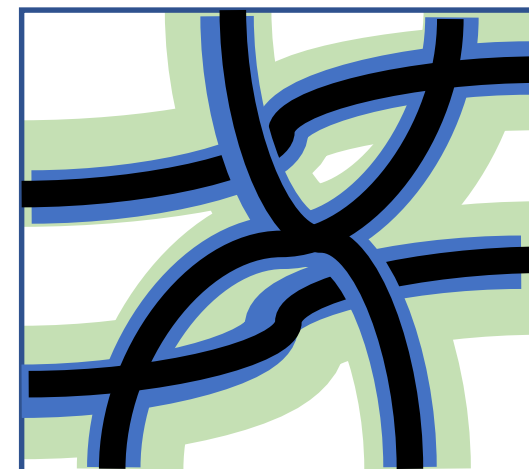
Porous substrate



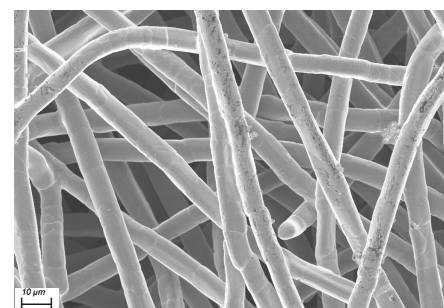
catalyst coated membrane (CCM),
e.g. powder-based catalyst layer







Catalyst coated substrate (CCS), e.g.
electrodeposited catalyst on substrate

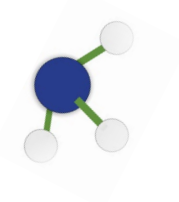


Carbon cloth



Stainless steel felt

-  Substrate, electric conductivity
-  Catalyst, electric conductivity
-  Ionomer, ionic conductivity
-  Void, gas transport



Model Details and Validation



Reaction Kinetics

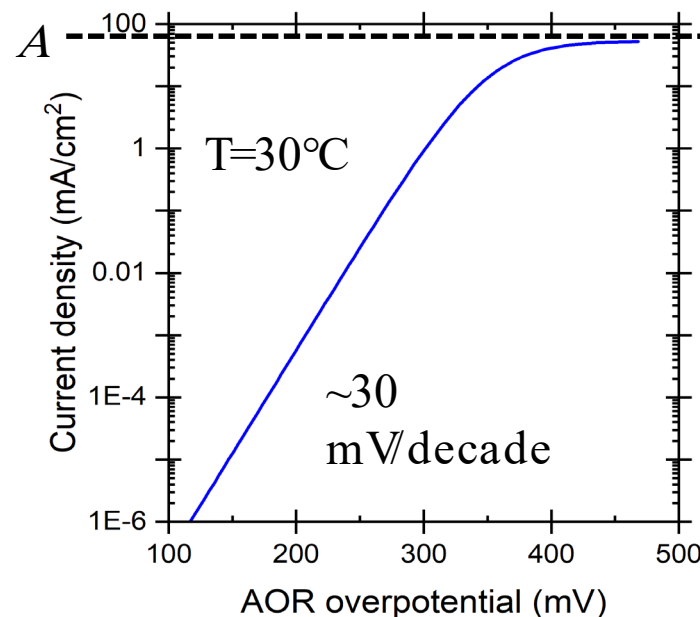


- ORR: Butler-Volmer with $\alpha_C=1.5$ [$p_{ref} = 3$ bar (absolute¹); $p^{0.5}$ based on²]

$$j = j_0^* \sqrt{\frac{p}{p_{ref}}} \left(e^{\frac{\alpha_A q_e \eta}{k_B T}} - e^{-\frac{\alpha_C q_e \eta}{k_B T}} \right)$$

- AOR: Same reaction mechanism assumed as by Zhao et al.¹, i.e. non- B-V kinetics (RLS: $2 \text{ NH}_2 \rightleftharpoons \text{N}_2\text{H}_4$)
 - Potential φ_0 , next slide

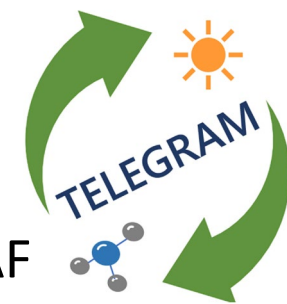
$$j = \frac{A \left(\frac{p_{\text{NH}_3}}{p_{ref}} \right)^2 e^{(2F/RT)(V-\varphi_0)}}{\left(1 + \frac{p_{\text{NH}_3}}{p_{ref}} e^{(F/RT)(V-\varphi_0)} \right)^2}$$



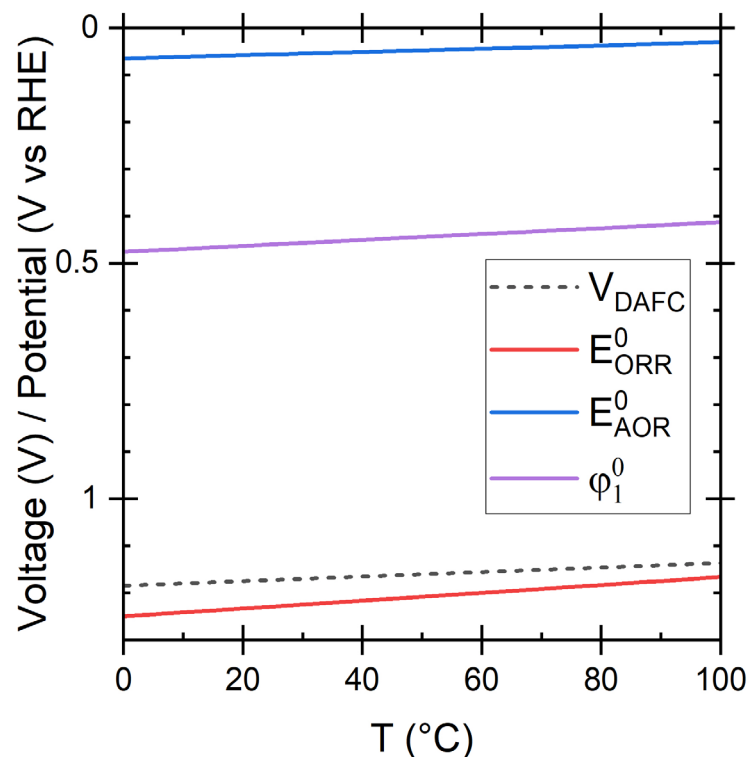
1. Zhao et al., ACS Energy Letters, 2021, 6, 1996-2002
2. Neyerlin et al., J. Electrochem. Soc. 2006, 153, A1955 – A1963



Reaction Potentials



- Temperature-dependent standard potentials, and thus cell voltage, based on NIST-JANAF thermochemical tables ³
- Nernst potentials for concentration/pressure effects



$$E_{AOR} = E_{AOR}^0(T) - \frac{RT}{6F} \ln \left(\frac{p_{NH_3}^2}{p_{N_2} p^0} \cdot a_{w,m}^{-6} \right)$$

$$E_{ORR} = E_{ORR}^0(T) + \frac{RT}{4F} \ln \left(a_{w,m}^2 \cdot \frac{p_{O_2}}{p^0} \right)$$

3. Chase, J Phys Chem Ref Data Monogr, 1998, 9, 1–1951



Water Uptake and Ionomer Conductivity



- Water uptake (from Gerhard et al. ⁴)

$$\lambda = \left(-0.6a_{w,ionomer}^3 + 0.85a_{w,ionomer}^2 - 0.2a_{w,ionomer} + 0.153 \right) (T - 313) + 39a_{w,ionomer}^3 - 47.7a_{w,ionomer}^2 + 23.4a_{w,ionomer} + 0.117$$

$$\lambda = \frac{c_w \cdot EW}{\rho_{ionomer}}$$

- Ionic conductivity, basis ⁴

$$\kappa_{OH^-} = \frac{20}{100} \left(0.1334 - 0.0003882T + (0.01148T - 3.9)a_{w,ionomer} - (0.0669T - 23)a_{w,ionomer}^2 + (0.1227T - 42.61)a_{w,ionomer}^3 - (0.06T - 21.8)a_{w,ionomer}^4 \right)$$

- S/cm, divided by 11.7 for AEM and by 7 for ionomer in catalyst layer to match Zhao et al. ¹

- Bruggemann model for the volume fraction of the ionomer, also for other transport phenomena

$$\kappa_{OH^-,eff} = \varepsilon_{ionomer}^{1.5} \kappa_{OH^-}$$

1. Zhao et al., ACS Energy Letters, 2021, 6, 1996-2002

4. Gerhardt et al., J. Electrochem. Soc., 2019, 166, F3180 – F3192



Water Transport, Transport of Diluted Species



- Continuation equation and flux

$$\nabla \cdot \vec{j}_W = R_W; \vec{j}_W = -D_W \nabla c_W - z \mu F c_W \nabla V$$

- Water diffusion coefficient ⁴

$$D_{H_2O,b} = 2.07 \cdot 10^{-7} \frac{\text{cm}^2}{\text{s}} \exp(3.95 a_{w,\text{ionomer}}) \cdot \exp\left(\frac{17.7 \frac{\text{kJ}}{\text{mol}}}{R} \left(\frac{1}{333} - \frac{1}{T}\right)\right)$$

- Electro-osmotic drag, 1 H₂O per 1 OH⁻

$$\vec{j}_{W,\text{drag}} = -\frac{\vec{i}}{F} = -z_W \mu_W F c_W \nabla \varphi_1 \rightarrow \mu_W = \frac{\kappa \text{OH}^-}{F^2 c_W}; \nabla V = \nabla \varphi_1$$

- Ionomer – gas boundary

$$R_{m,\text{gas}} = -K(a_{w,\text{ionomer}} - a_{w,\text{gas}}); a_{w,\text{gas}} = \text{RH} = \frac{p_{H_2O}}{p_W}$$

- AOR produces water ($R_W > 0$), ORR consumes it ($R_W < 0$)

4. Gerhardt et al., J. Electrochem. Soc., 2019, 166, F3180 – F3192



Gas Convection, Darcy's Law



- Darcy's law and Carman-Kozeny

$$\vec{u} = -\frac{\kappa}{\mu} \nabla p; \kappa = \frac{\varepsilon_{\text{void}}^3 d^2}{16k_K (1 - \varepsilon_{\text{void}})^2}$$

- Total pressure, Wexler's ⁵ formula for vapor equilibrium pressure

$$p_A = p_{\text{dry}} + \text{RH} p_w;$$

$$p_w = \exp(-2.9912729 \cdot 10^3 T^{-2} - 6.0170128 \cdot 10^3 T^{-1} + 1.887643845 \cdot 10^1 - 2.8354721 \cdot 10^{-2} T + 1.7838301 \cdot 10^{-5} T^2 - 8.4150417 \cdot 10^{-10} T^3 + 4.4412543 \cdot 10^{-13} T^4 + 2.858487 \ln T)$$

- Viscosity, Wilke's model ⁶, mass fraction x_j from Transport of Concentrated Species (next slide)

$$\mu = \frac{\sum_j^n \frac{x_j \mu_j}{\sum_i^n x_i \varphi_{ji}}}{\sqrt{8 \left(1 + \frac{M_j}{M_i}\right)}}; \varphi_{ji} = \frac{\left(1 + \sqrt{\frac{\mu_j}{\mu_i} \left(\frac{M_i}{M_j}\right)^{1/4}}\right)^2}{\sqrt{8 \left(1 + \frac{M_j}{M_i}\right)}}$$

- Comsol's built-in model for viscosity coefficients (ideal gas), $\mu_j \approx \mu_j^* \left(\frac{T}{T^*}\right)^{0.76}$

5. Wexler, Journal of Research of the National Bureau of Standards Section A: Physics and Chemistry, 1976, 80A, 775

6. Wilke, J. Chem. Phys., 1950, 18, 517-519



Maxwell-Stefan Diffusion, Transport of Concentrated Species



- Continuation equation, steady-state

$$\nabla \cdot \vec{j}_i + \rho(\vec{u} \cdot \nabla)\omega_i = R_i$$

- Fluxes

$$\vec{j}_i = -\rho\omega_i \sum_{k=1}^Q \tilde{D}_{ik} \vec{d}_k$$

- Driving force

$$\vec{d}_k = \nabla x_k + \frac{1}{p_A} [(x_k - \omega_k) \nabla p_A]$$

- x_k mass fraction, ω_k volume fraction

- Binary diffusion coefficient, Fuller-Schettler-Giddings ⁷

$$D_{AB} = \frac{1.01325 \cdot 10^{-2} T^{1.75} \sqrt{\frac{1}{M_A} + \frac{1}{M_B}}}{p \left[(\sum_A v)^{1/3} + (\sum_B v)^{1/3} \right]^2}$$

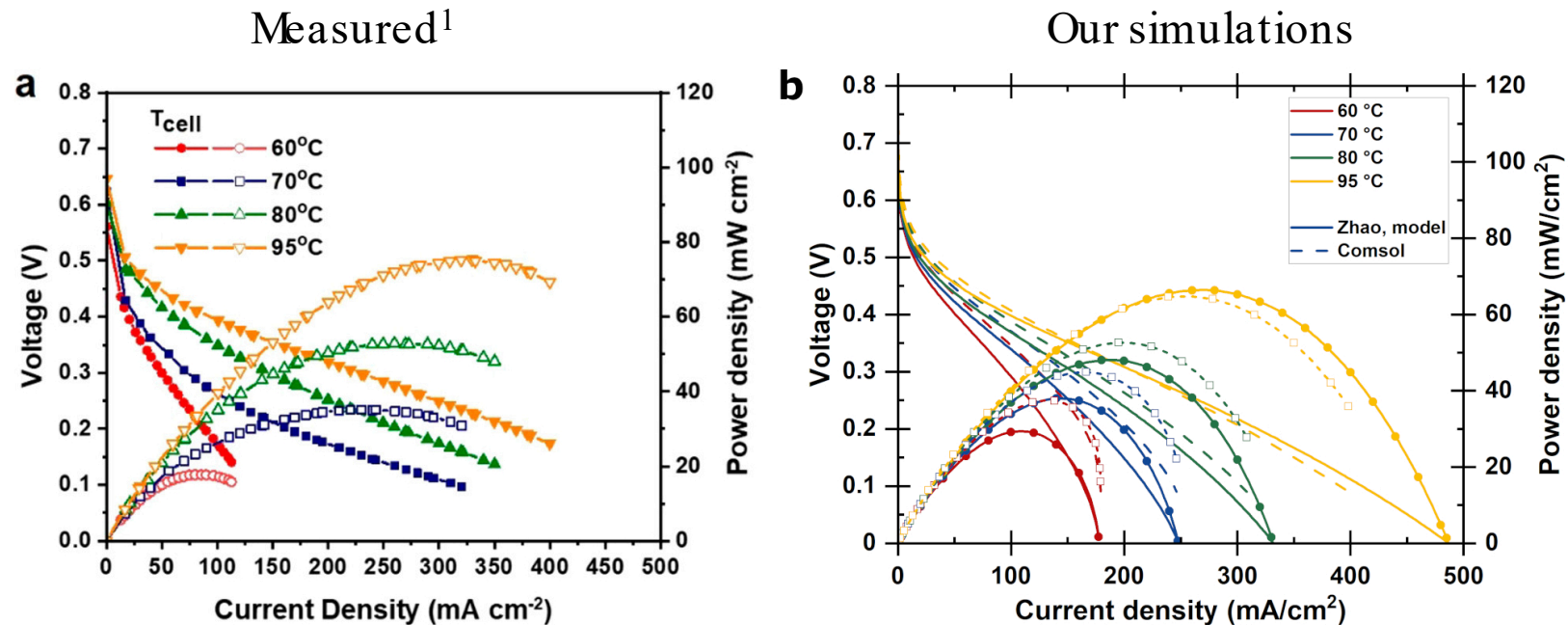
- Pressure in Pa

Molecule	Volume ($\sum_i v$)
H ₂ O	13.1
NH ₃	20.7
O ₂	16.3
N ₂	18.5

7. Fuller, Schettler and Giddings, Ind. Eng. Chem., 1966, 58, 18-27



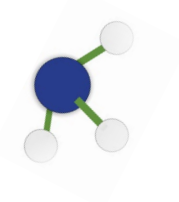
Validation of Gas-fed DAFC Model



- Transport model with Comsol multiphysics verified against simpler model from literature¹ that was verified against measurements
- Perfect match at all temperatures impossible due to different temperature dependencies of ionomer conductivity (¹ vs ⁴), for later simulations ionic conductivity optimized for best match at 75 °C

1. Zhao et al., ACS Energy Letters, 2021, 6, 1996-2002

4. Gerhardt et al., J. Electrochem. Soc., 2019, 166, F3180 – F3192

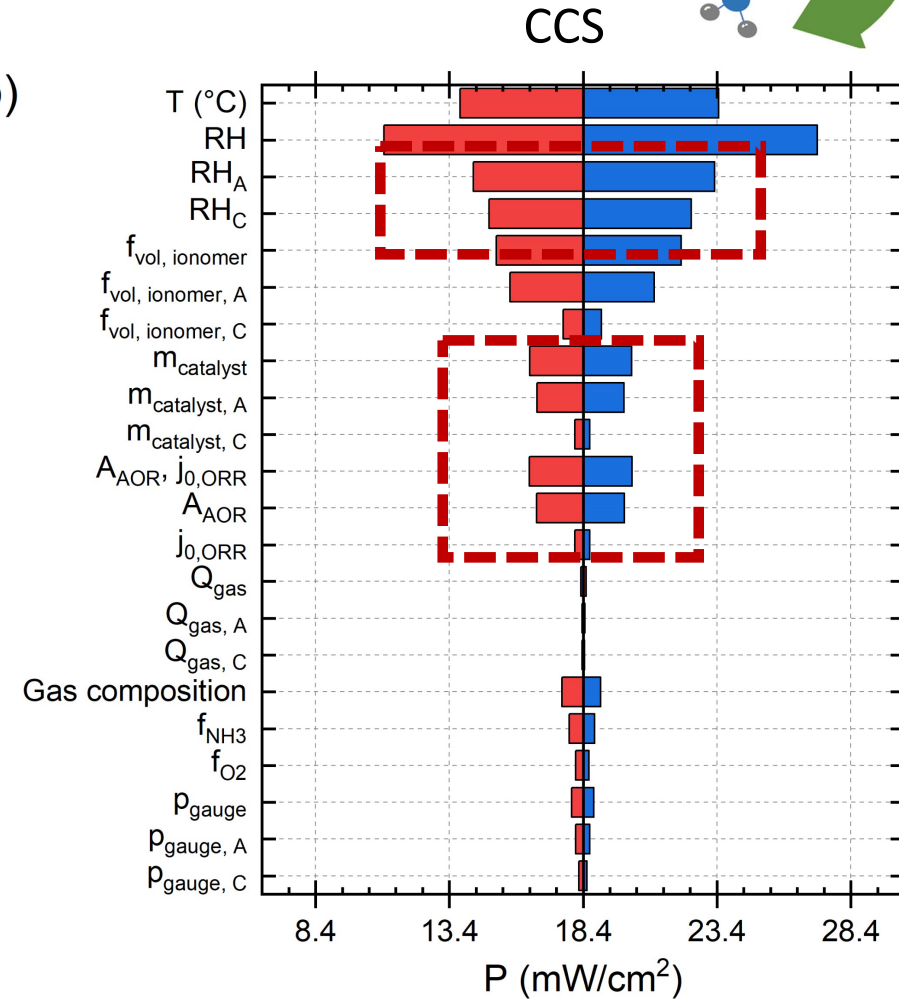
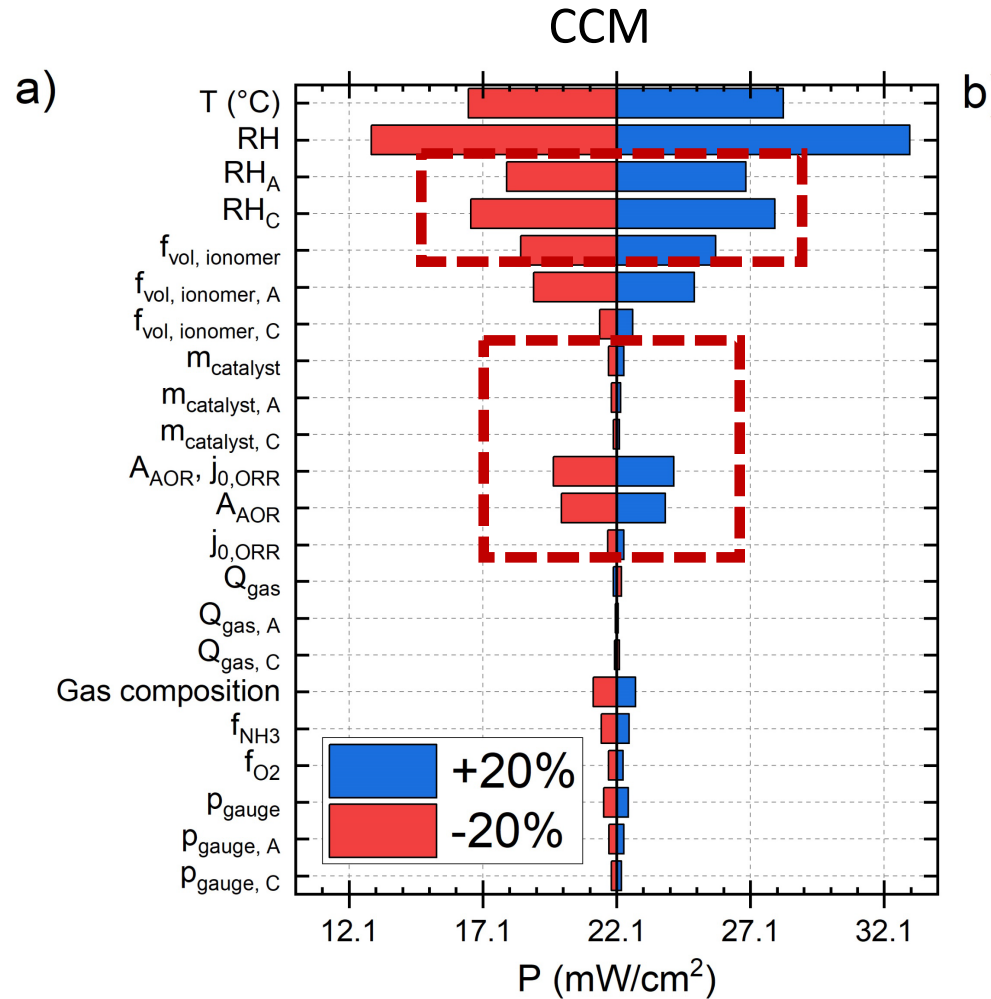


Sensitivity Analysis and Physical Operation



Effect of the Parameters on Power Output

- Catalyst loading has almost no effect on CCM
- Generally, DAFC is more sensitive to the anode than to the cathode, especially with catalysts, except CCM & RH
- Pressure can be more useful than this comparison indicates

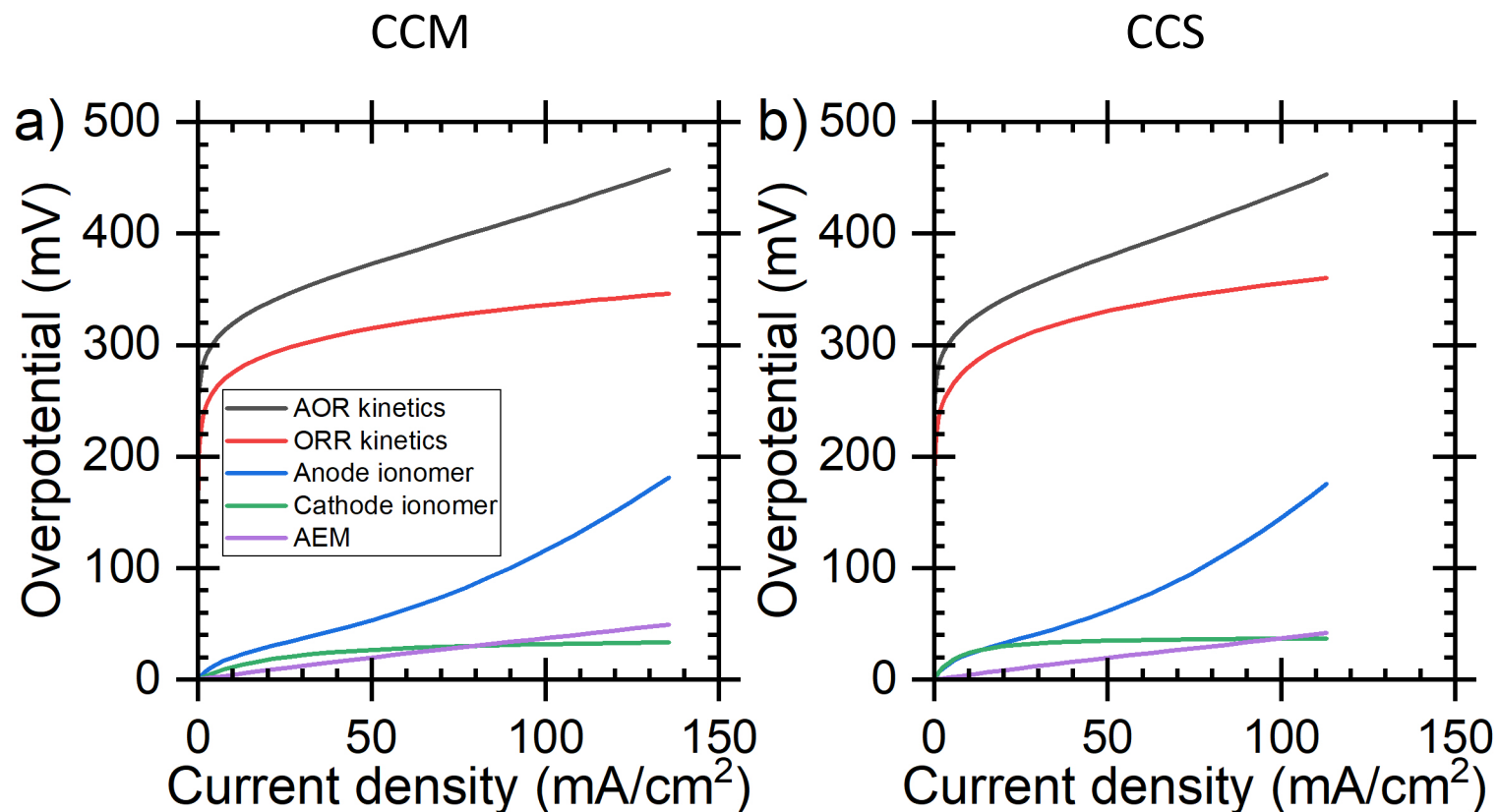




Losses at anode increase faster than at cathode



- Voltage losses vs current density at the baseline, the same general sensitivity pattern remains with other parameters
- Differences in anode vs cathode ionomer losses are due to different reaction kinetics, thus different spatial rate distribution

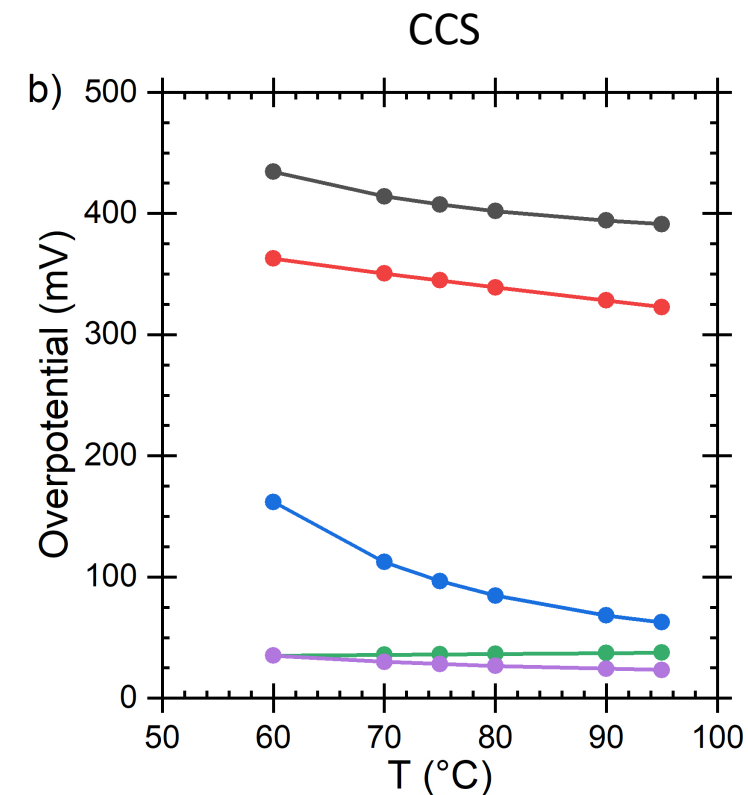
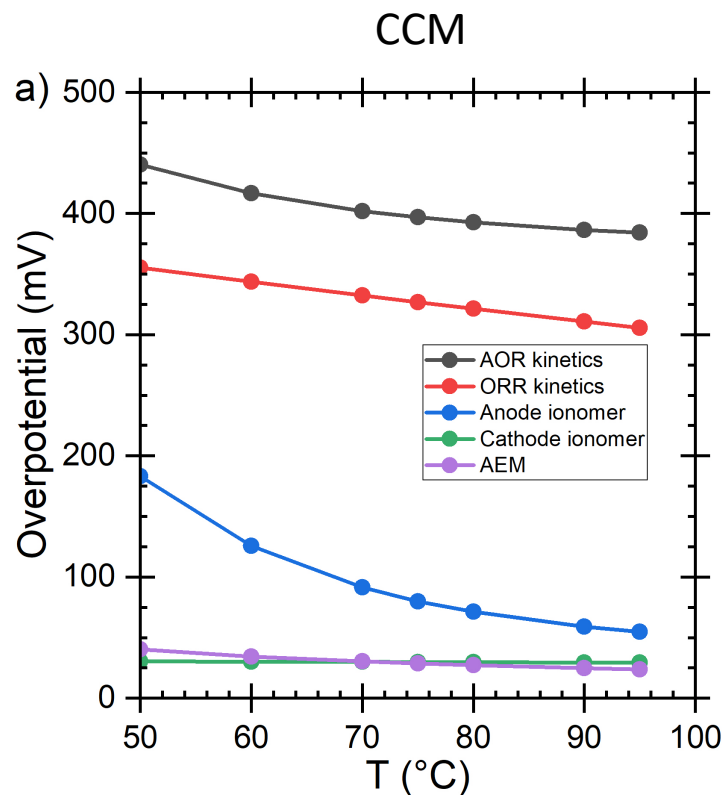




Anode ionomer losses are the most sensitive to temperature

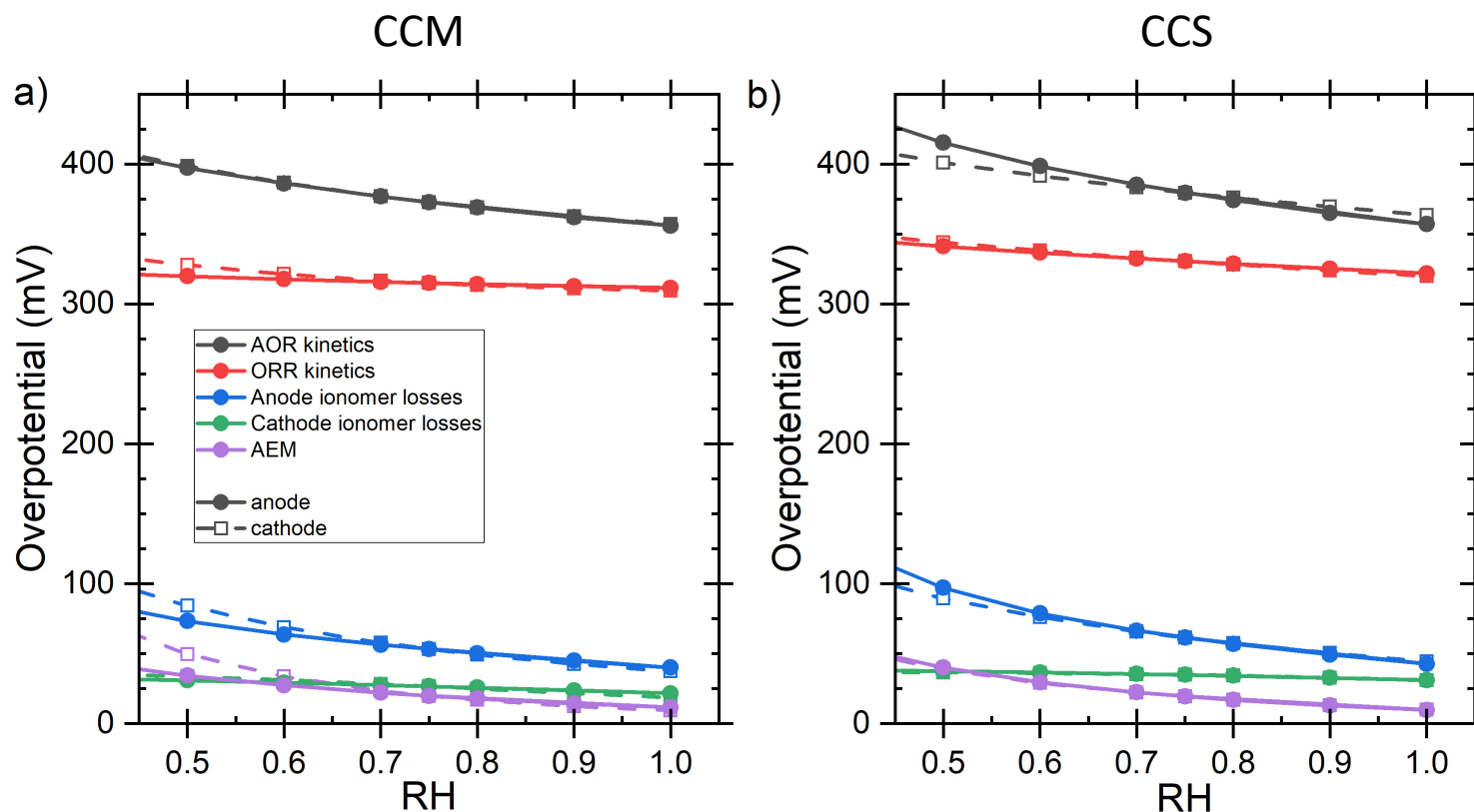


- 75 mA/cm² ; CCS was limited to lower currents at 50 °C
- Anode ionomer losses are the most sensitive loss component
- Below 75 °C DAFC even more sensitive to anode, above it ORR has a larger effect than AOR

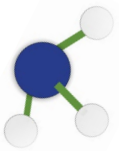




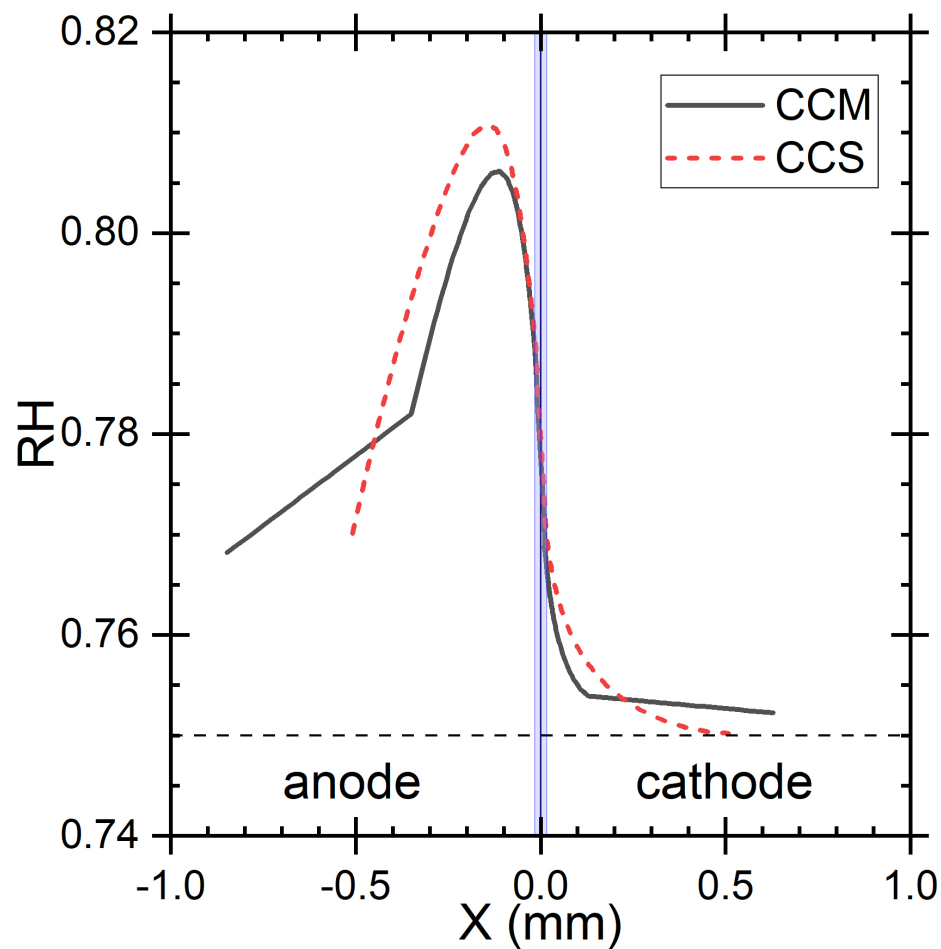
Relative Humidity



- 75 mA/cm²
- Different sensitivities to anode and cathode RH are due to AOR, AEM and anode ionomer sensitivities
- CCM cathode is the thinnest ionomer & catalyst layer which is likely important for the increased sensitivity



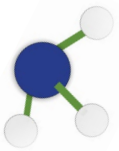
Most of generated water exists from anode



- RH/water activity in DAFC at 90 mA/cm² (CCM: 0.25 V, CCS: 0.19 V), profile matches literature, e.g.^{4,8}
- Maximum RH in anode, higher in CCS than in CCM
- Less water exits from cathode in CCS, which could partially explain the stronger effect of cathode RH on CCM
 - Thinner cathode CL in CCM helps back diffusion

4. Gerhardt et al., J. Electrochem. Soc., 2019, 166, F3180 – F3192

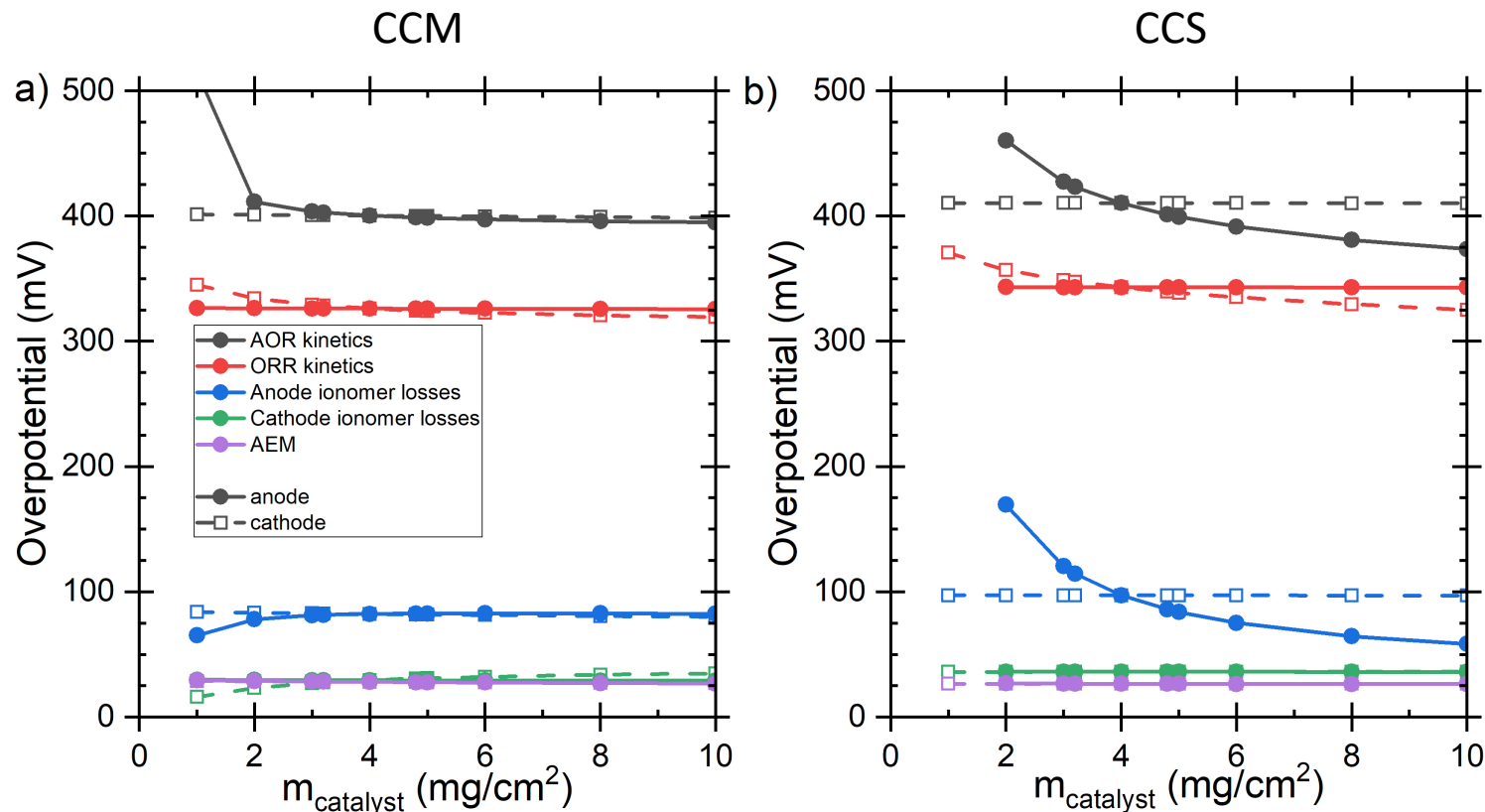
8. Omasta et al., Energy Environ. Sci., 2018, 11, 551-558



Catalyst Loading



- 75 mA/cm²
- CCS is almost identical to the effect of catalyst activity
 - Catalyst loading per volume/thickness increased, constant layer thickness
 - Anode ionomer losses follow kinetics but not cathode; different kinetics
- Increasing loading in CCM increases CL thickness
 - Ionomer losses are increased, offset gains in kinetics at over ca. 2-3 mg/cm²





Conclusions



- AOR and ORR kinetics are the biggest voltage loss components, must be reduced for high performance
- Anode losses are typically more sensitive than cathode; improving anode has a higher impact on DAFC performance
 - AOR is often the most sensitive loss component but not always
 - Anode ionomer losses magnify the effect of AOR kinetics (vs ORR kinetics), sometimes even the most sensitive component
 - Reaction mechanism and possible changes in Tafel slope affect electrode response to conditions, with different AOR and ORR kinetics the cathode could be more important than the anode
- As temperature and CCM & RH show, cathode properties could sometimes be more important than the anode properties



Thank you for your attention!



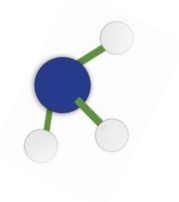
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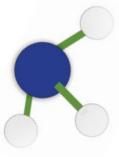


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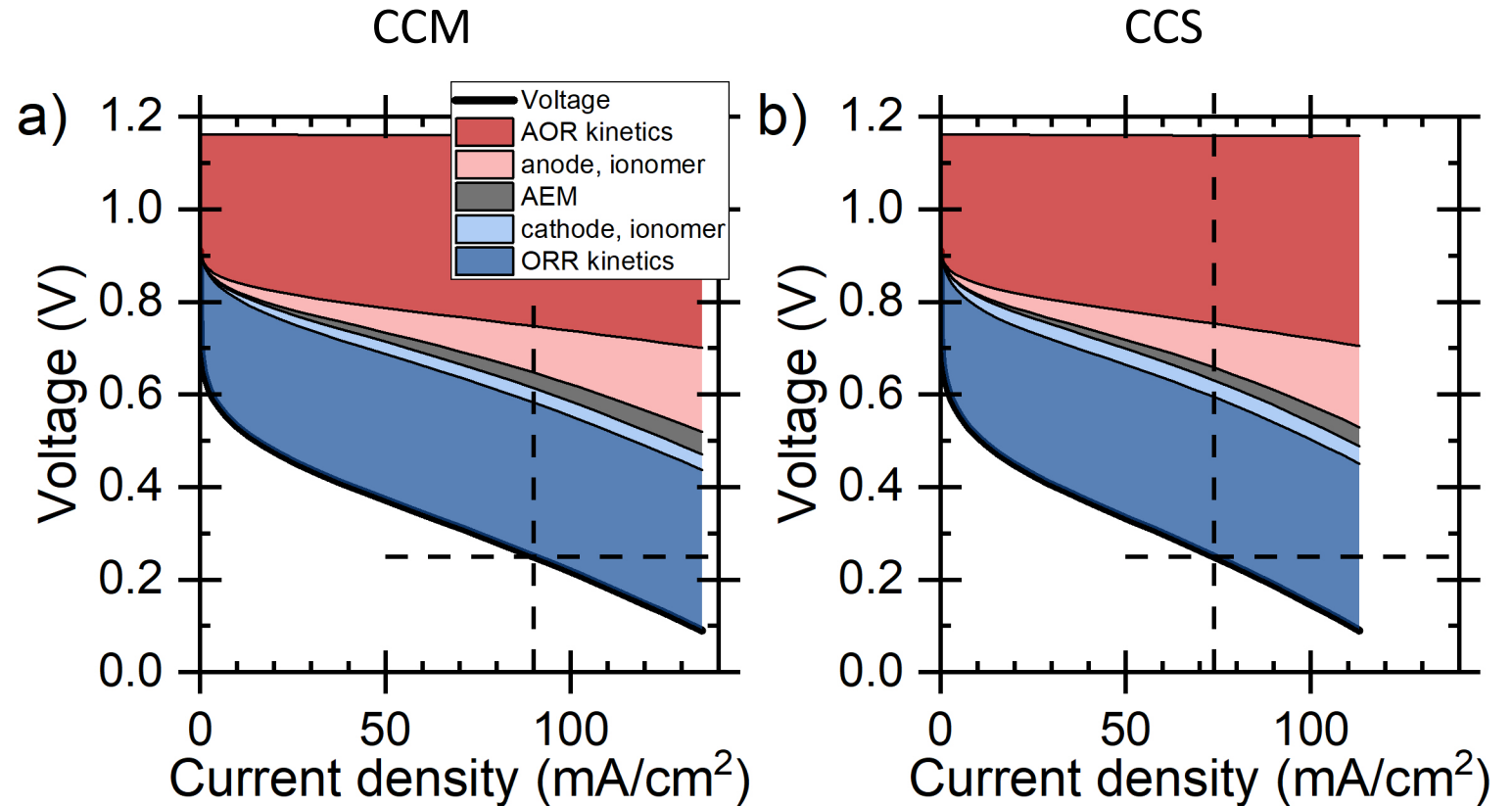
Extra slides



Reaction kinetics are the largest losses



- Voltage losses at the baseline scenario
- There are other minor losses, such as substrate electric resistance, but these are the 5 main components
- Comparisons for power at 0.25 V (dashed lines) or at 75 mA/cm² current density

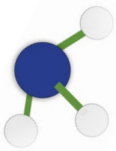




Sensitivity analysis

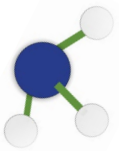


- DAFC operating parameters varied by 20 % from baseline to determine the relative importance of different parameters
 - Power at 0.25 V (near the maximum power at baseline) used for the comparisons
- Comparison of voltage losses at selected current density (mostly 75 mA/cm²) to determine the reasons for observed sensitivities, and their differences



Baseline parameters and ranges

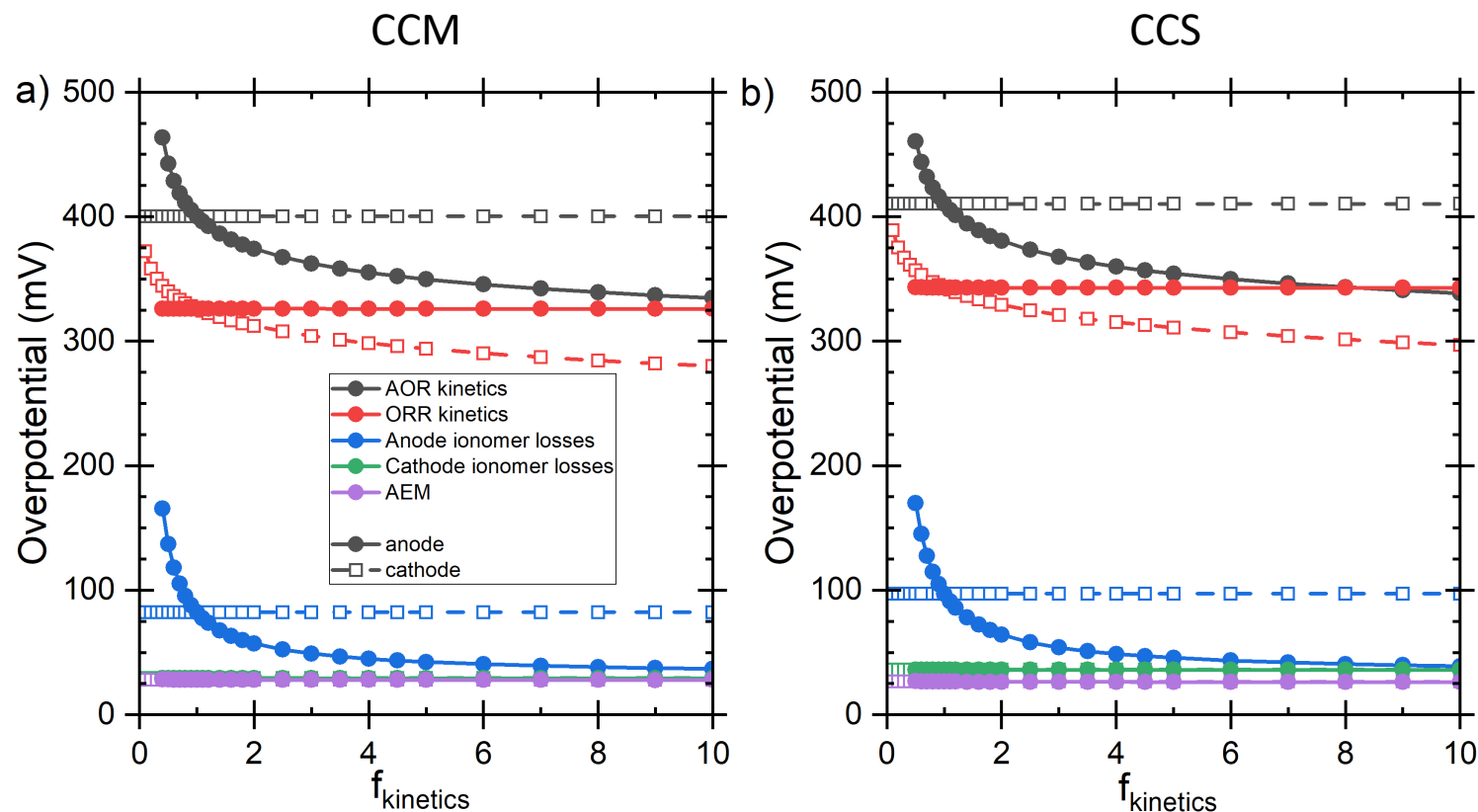
Parameter and unit	Model validation (earlier)	Baseline [and sensitivity analysis range]
T (°C)	60 – 95	75 [60 – 90]
Relative humidity	1	0.75 [0.6 – 0.9]
Anode catalyst loading (mg/cm ²)	4	4 [3.2 – 4.8]
Cathode catalyst loading (mg/cm ²)	3	4 [3.2 – 4.8]
Anode gauge pressure (bar)	0	1 [0.8 – 1.2]
Cathode gauge pressure (bar)	2	1 [0.8 – 1.2]
Ionomer volume fraction	0.85	0.75 [0.6 – 0.9]
Anode gas flow rate (ml/(min cm ²))	160	100 [80 – 120]
Cathode gas flow rate (ml/(min cm ²))	100	100 [80 – 120]
Anode NH ₃ fraction	0.5	0.5 [0.4 – 0.6]
Cathode O ₂ fraction	1	0.5 [0.4 – 0.6]

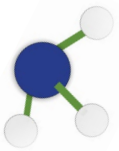


Catalyst activity

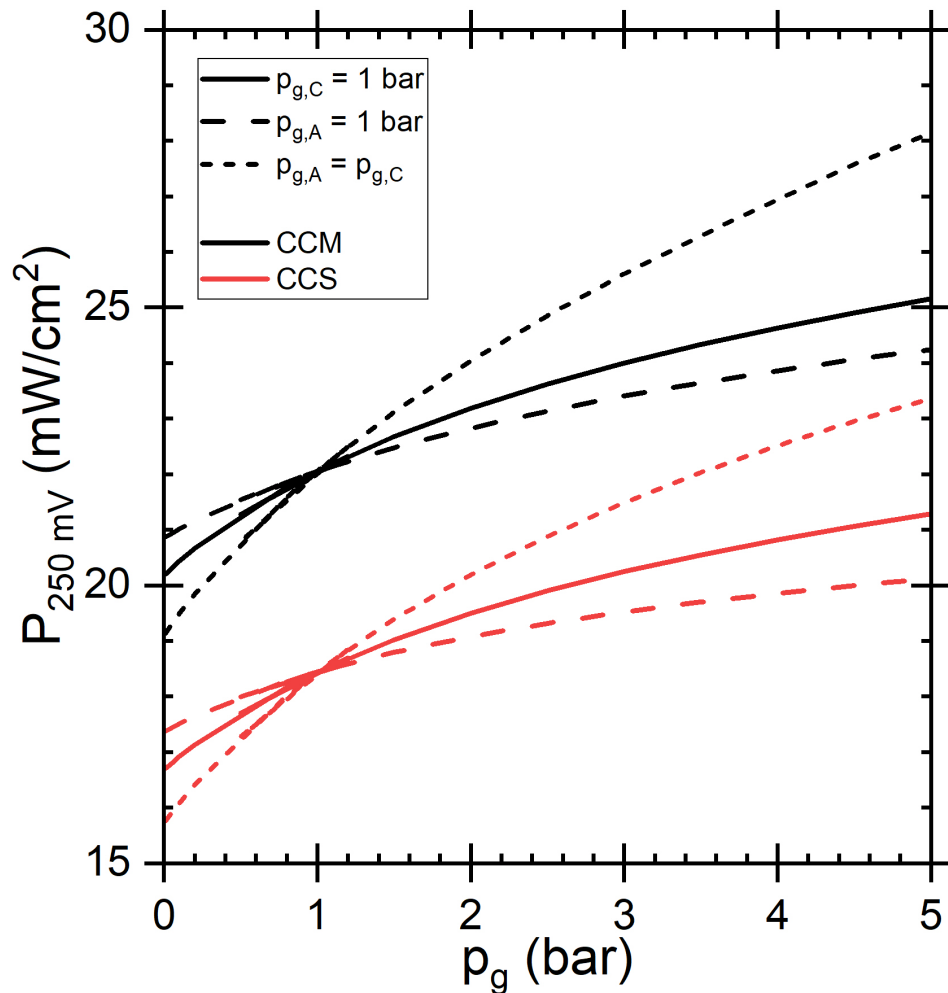


- 75 mA/cm²
- No significant differences CCM vs CCS
- Anode ionomer losses follow AOR kinetics!

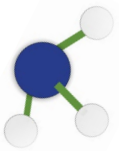




Pressure



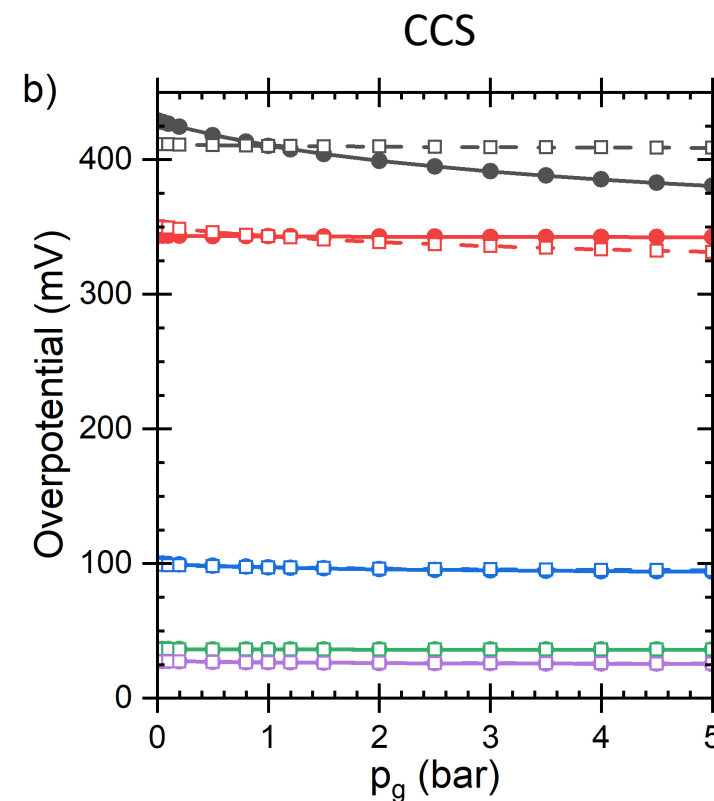
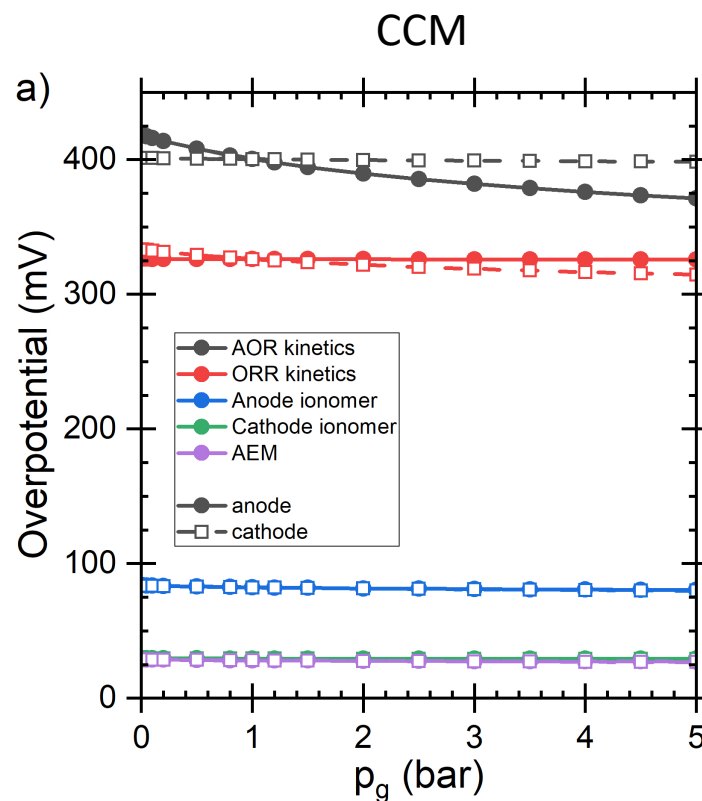
- Pressure multiplication allows increasing power as much as increasing temperature or RH
- DAFC is more sensitive to anode pressure than to cathode pressure because pressure mainly affected kinetic overpotentials

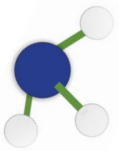


Pressure



- 75 mA/cm²
- No significant differences CCM vs CCS
- Only reaction kinetics are noticeably affected

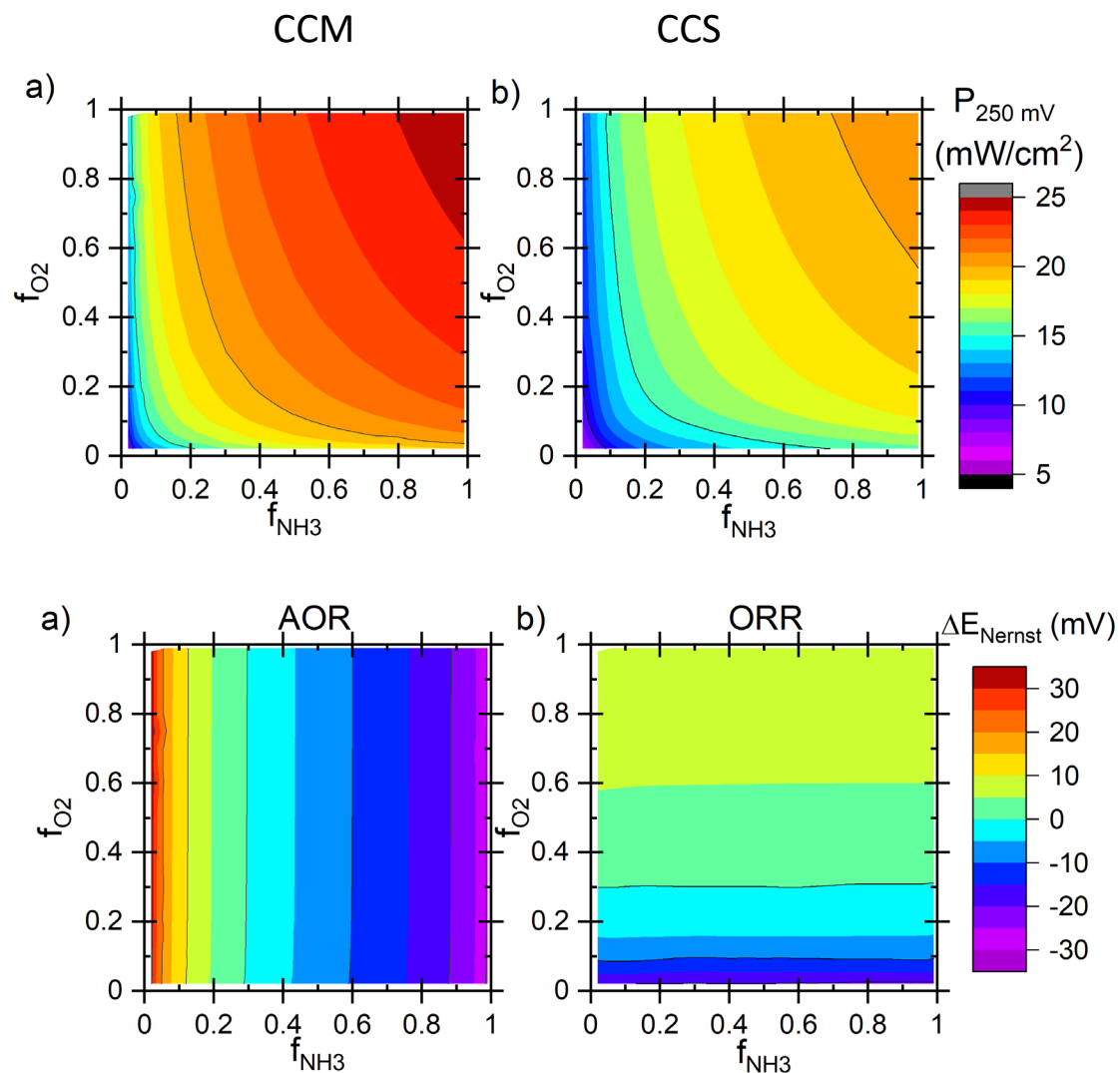




Gas composition



- Overall higher power with CCM, no other significant differences CCM vs CCS
- Ammonia more important than oxygen, larger effect on Nernst voltage (although slightly magnified by the use of N_2 as the inert gas component)





Concurrent change in all parameters



- Power density at 0.25 V
- No significant differences CCM vs CCS
- Higher power increase than separate 20 % changes indicate, and smaller decrease
- Gas transport limitation with too much ionomer

