A phase field study on the microstructure evolution in SOFC anode under operating condition: comparison between $Ni(OH)_2$ diffusion and Ni-YSZ wettability change.

Yinkai Lei [1,2], Tian-Le Cheng [1,2], Harry Abernathy [1,2] , Thomas Kalapos [1,2], Gregory Hackett [1], Youhai Wen [1]

[1]US Department of Energy, National Energy Technology Laboratory, Pittsburgh, PA /Morgantown, WV / Albany, OR; [2]Leidos Research Support Team, Pittsburgh, PA / Morgantown, WV / Albany, OR

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Background

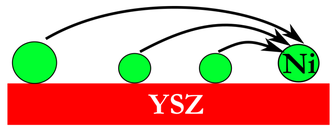
- Microstructure evolution in Ni-YSZ anode causes performance degradation.
- Two types of microstructure evolutions

Ni coarsening

Average particle size growth at the expense of small particles

Ni redistribution

Directional migration of Ni



- Both are sensitive to operating conditions
- Mechanisms are not clear, candidates: $Ni(OH)_2$ diffusion [1] and Ni-YSZ wettability change [2]

Phase-field model

- Kim-Kim-Suzuki model + $Ni(OH)_2$ diffusion-reaction

$$\frac{\partial c_{Ni}}{\partial t} = \nabla \cdot \left\{ D_{Ni} \left[\nabla c_{Ni} - \frac{dh_c}{d\phi} \left(c_{Ni}^e - c_{Ni}^p \right) \nabla \phi \right] \right\} - S$$

$$\frac{\partial \phi}{\partial t} = M_\phi \left\{ \kappa \nabla^2 \phi - \rho \frac{df}{d\phi} - \frac{dh_p}{d\phi} \left[G^e(c_{Ni}^e) - G^p(c_{Ni}^p) - \left(c_{Ni}^e - c_{Ni}^p \right) \frac{\partial G^e(c_{Ni}^e)}{\partial c} \right] \right\}$$

$$\nabla \cdot \left\{ D_{Ni(OH)_2} \left[\nabla c_{Ni(OH)_2} + \frac{dh_s}{d\phi} \frac{k_f(P_{H_2O})}{k_d(P_{H_2O})} c_{Ni}^e \nabla \phi \right] \right\} + S = 0$$

$$S = [1 - h_s(\phi)] k_f(P_{H_2O}) h_s(\phi) c_{Ni}^e - k_d(P_{H_2O}) h_s(\phi) c_{Ni(OH)_2}$$

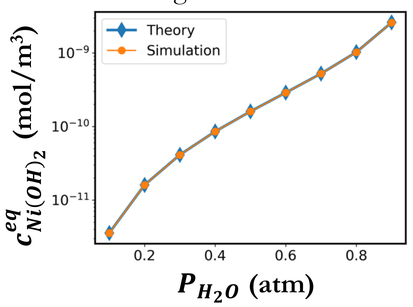
c_{Ni}: Ni concentration, $c_{Ni(OH)_2}$: $Ni(OH)_2$ concentration, ϕ: phase order parameter, 1 – Ni, 0 – Pore.

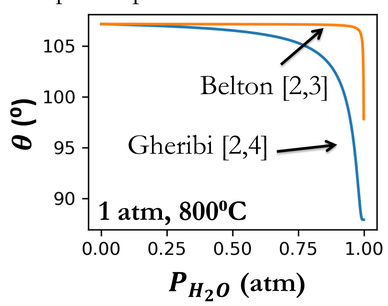
- Ni-YSZ wettability control: boundary condition on Ni-YSZ interface

$$-\kappa(\nabla\phi \cdot \vec{n}) = -6\gamma\phi(1-\phi)\cos\theta$$

θ: Ni-YSZ contact angle, γ: Ni surface energy.

- Both the equilibrium concentration of $Ni(OH)_2$ and the Ni-YSZ contact angle are functions of steam partial pressure.

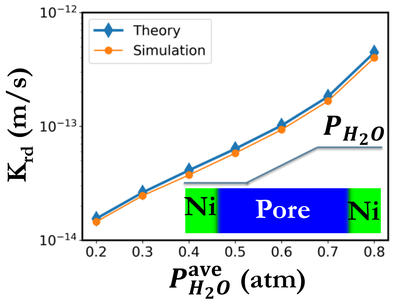




Model validation

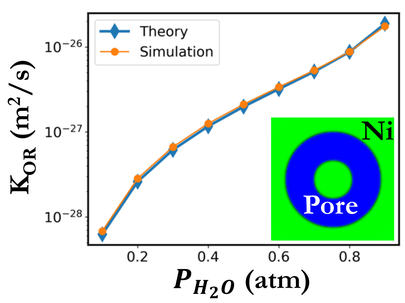
- Ni redistribution: fixed 0.2 atm difference in p_{H_2O}

$$z = z_0 + K_{rd} t$$

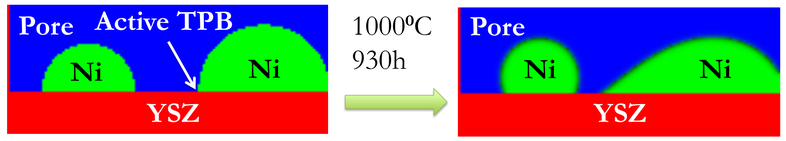


- Ni coarsening: constant p_{H_2O}

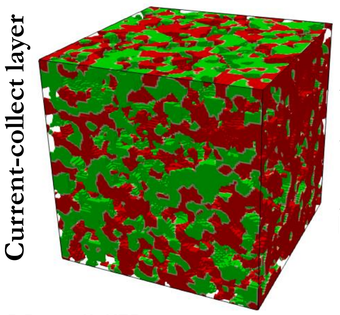
$$\frac{dS}{dt} = -\frac{K_{OR}}{\ln r_1 - \ln r_2} \frac{r_1 + r_2}{r_1 r_2}$$



- Ni-YSZ wettability control : Change the Ni-YSZ contact angle near active TPB from 117° to 25°



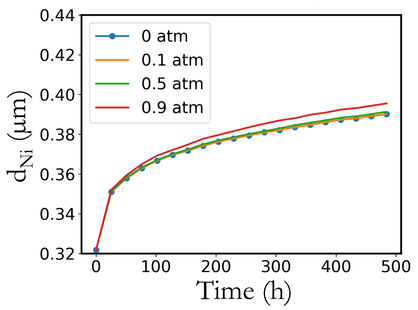
Results

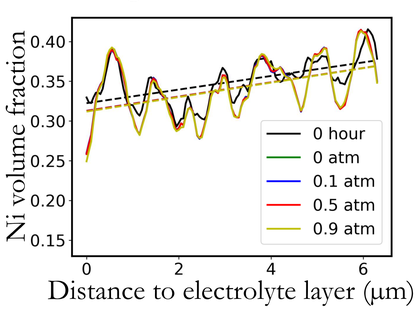


- 35%YSZ-35%Ni-30%Pore
- Initial Ni diameter: ~0.32 μm
- 800°C up to 500 hours.
- Overall gas pressure: 1 atm
- Near OCV: uniform steam partial pressure.
- Under load: Steam partial pressure linearly decrease from electrolyte layer to current-collect layer.

Near OCV

- Uniform steam partial pressure
- Ni(OH)2 diffusion: slightly faster coarsening and no redistribution.

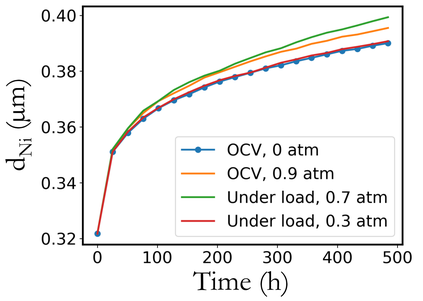


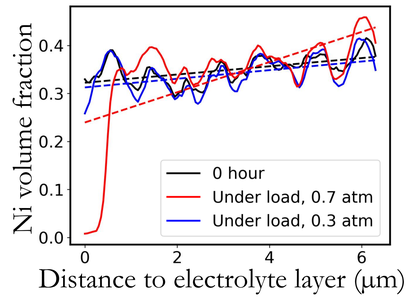


- Ni-YSZ wettability change: Negligible effect due to small and uniform contact angle change.

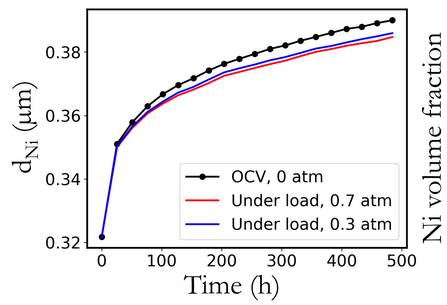
Under load

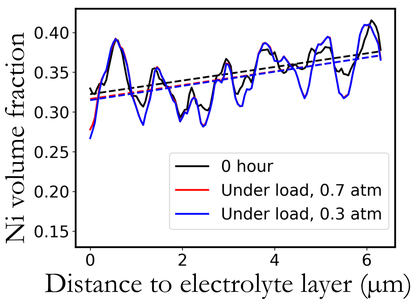
- 0.4 atm difference between electrolyte and current-collect layer.
- Average steam partial pressure: 0.3 atm (high fuel supply) and 0.7 atm (low fuel supply)
- $Ni(OH)_2$ diffusion: slightly faster coarsening and redistribution from electrolyte layer to current-collect layer.





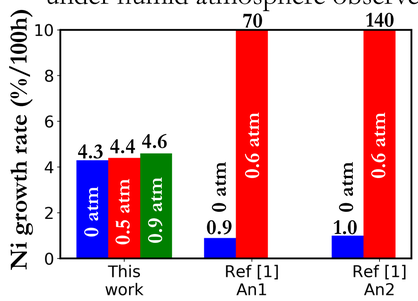
- Ni-YSZ wettability change: Slightly slower coarsening and no visible redistribution

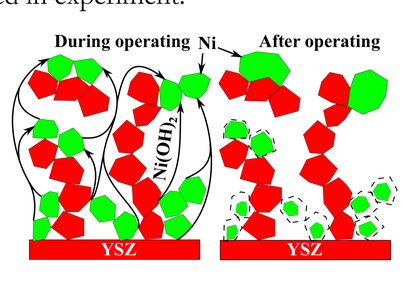




Comparison to experiments

- $Ni(OH)_2$ diffusion is not likely the reason for the fast coarsening under humid atmosphere observed in experiment.





- $Ni(OH)_2$ diffusion drives Ni away from the electrolyte layer, which is consistent with some experiments [5,6].
- Ni-YSZ wettability change is not likely to cause Ni redistribution under current understanding.

References:

[1] Holzer et al, J Power Sources, 196 (2011) 1279-1294 [2] Jiao et al, J Power Sources, 396 (2018) 119-123
[3] Belton, Metall. Trans. B, 7B (1976) 35 [4] Gheribi et al, J. Non-Crystall. Solids, 505 (2019) 154-161
[5] Sciazko et al, J Electrochem Soc, 166 (2019) F44-F52 [6] Zekri et al, Fuel Cells, 17 (2017) 359-366

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