Modeling Ni Coarsening Under Humid Atmosphere in the Electrode of Solid Oxide Cells

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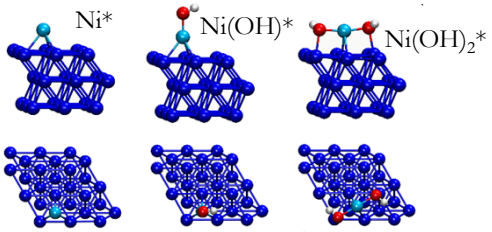
Background

- Ni coarsening is known to be faster under humid atmosphere [1].
- It is attributed to the formation of $Ni(OH)_x$ under humid atmosphere.
- Our previous work shows that gas-phase diffusion of $Ni(OH)_2$ in pore phase is unlikely to cause fast Ni coarsening under humid atmosphere.
- Surface diffusion of $Ni(OH)_x$ (x=1, 2) on the most stable Ni surface, Ni (111), is checked in this work.

Methodology

Density-Functional Theory Calculations

- Vienna Ab initio Simulation Package
- Revised Perdew-Burke-Ernzerhof (RPBE) functional
- Projector Augmented-Wave method
- Used for evaluating the free energy of formation and the diffusion barrier of Ni*, Ni(OH)*, and $Ni(OH)_2$*



Surface coverage:

Free energy of formation

$$\theta_i = \exp\left(-\frac{\Delta G_i^f}{RT}\right), i = \mathrm{Ni}^*, \mathrm{Ni(OH)}^*, \mathrm{Ni(OH)}_2^*$$

Diffusion of single atom or molecule:

Diffusion barrier

$$D_i^0 = f_i^0 \exp\left(-\frac{\Delta E_i^b}{RT}\right), i = \mathrm{Ni}^*, \mathrm{Ni(OH)}^*, \mathrm{Ni(OH)}_2^*$$

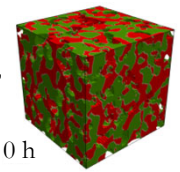
Prefactor from computed vibrational frequencies

Diffusivity of i is $D_i = \theta_i D_i^0$

Phase-Field Modeling

- Simplified Kim-Kim-Suzuki model [2]
- Surface diffusivity of Ni evaluated from DFT calculations

$$D_{\mathrm{Ni}}^{\mathrm{surf}} = \sum_i \theta_i D_i^0,$$

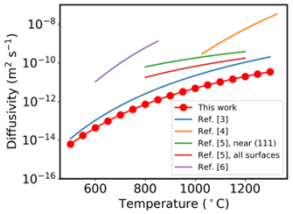


- Binary gas of steam and hydrogen with $p_{\mathrm{total}} = 1$ atm

Model Validation

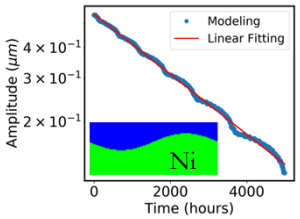
Density-Functional Theory Calculations

The calculated surface diffusivity of Ni agrees well with previous computation [3] and experiments [4-6].



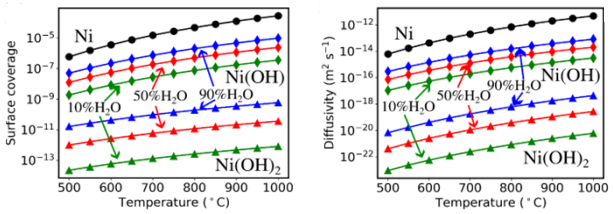
Phase-Field Modeling

The modeled decrease in the amplitude of sinusoidal surface agrees well with theory [7].
The slope of logarithm of amplitude:
Linear fit: $0.8 \times 10^{-7}\ s^{-1}$
Theory: $1.2 \times 10^{-7}\ s^{-1}$



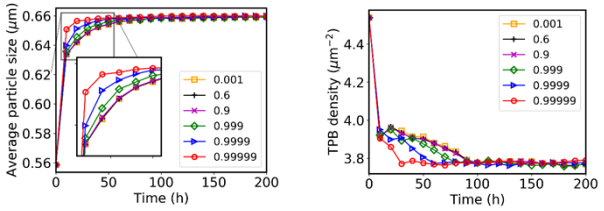
Results

Surface Coverage and Diffusivity



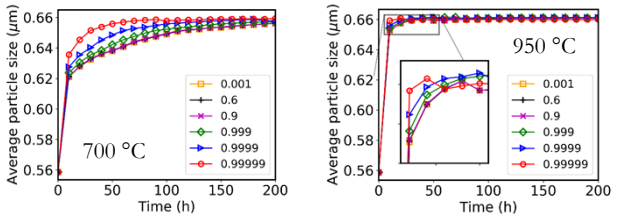
Both the surface coverage and diffusivity of $Ni(OH)_x$ are orders of magnitude lower than Ni adatoms when $p_{H_2O} \leq 0.9$ atm.

Effect of Steam Partial Pressure



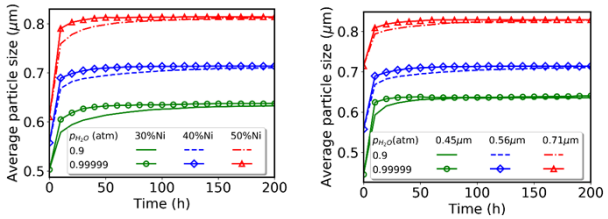
At 800 °C, Ni coarsening and triple-phase boundary (TPB) degradation is only significantly faster when $p_{H_2O} \geq 0.9999$ atm.

Effect of Temperature



Ni coarsening is faster at higher temperature, but the effect of steam partial pressure is the same at different temperatures.

Effect of Initial Microstructure

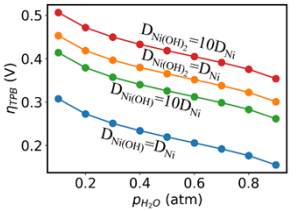


The effect of steam partial pressure is similar for different initial microstructures.

Discussion

A large overpotential in fuel cell mode may result in an Ni(OH) surface diffusivity greater than Ni surface diffusivity.

The fast Ni coarsening under humid atmosphere is unlikely to be explained by the effect of steam partial pressure or microstructure alone. A large overpotential is essential to cause a fast Ni coarsening.



References:
[1] Holzer, *et al.*, J. Power Sources **196** (2011) 1279-1294; [2] Lei *et al.*, J. Power Sources, **545** (2022) 231024.
[3] Nakao, *et al*, J. Phys. Chem. C, **120** (2016) 16641-16648; [4] Azzerri & Colombo, Metallogr. **9** (1976) 233-244;
[5] Blakely & Mykura, Acta Metall. Mater. **9** (1961) 23-31; [6] Wolfe, PhD. Dissertation, Univ. Missouri-Rolla. 1968;
[7] Balluffi, *et al.*, Kinetics of Materials, Wiley, 2005.