Effects of Microstructural Variability and Operating Conditions on Cr-poisoning in Solid Oxide Fuel Cell Cathodes Using High-Performance Computing Simulations

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Motivation

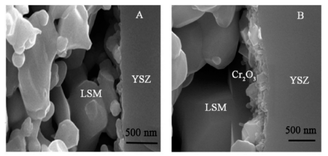
Key factors preventing widespread commercialization for SOFC

1. Durability, 2. Reliability, 3. Cost

Electrode microstructures affect these!

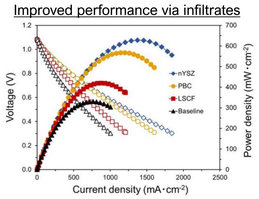
- **Cr poisoning** is one major degradation mechanism (durability)
- Infiltration is a processing method to improve microstructures
- Infiltration is thought to increase resistance to Cr poisoning
- **Challenge** : complex electrodes, long lifetimes inhibit study

Chromium poisoning image



Solid State Ionics 354 (2020): 115410.

Improved performance via infiltrates

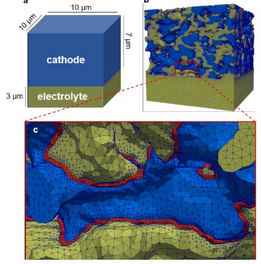


Journal of The Electrochemical Society 167.2 (2020): 024517.

Can we explore Cr poisoning inside complex microstructures?

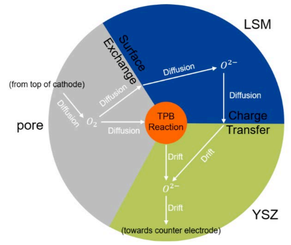
- We can simulate electrochemical performance using HPC
- ERMINE is a FEM code to simulate three phase cathodes
- We have implemented a standard tpb Cr-poisoning model

Volumetric meshed microstructure



Electrochimica Acta 345 (2020), 136191.

ORR pathways implemented in ERMINE



MethodsX 7 (2020): 100822.

Cr poisoning model for Electrochemical Reactions in Microstructural Networks

Implementing chromium poisoning from: [1]Miyoshi et al., Journal of Power Sources 326 (2016): 331-340.

Electrochemical reaction for Cr poisoning: $2CrO_2(OH)_{2(g)} + 6e^- \rightarrow Cr_2O_{3(s)} + 2H_2O + 3O^{2-}$

Chromium deposition (i_{D,Cr_2O_3}) is driven by local overpotential at triple phase boundaries (η_{tpb}): [1]

$$i_{D,Cr_2O_3}\left[\frac{A}{cm^2}\right] = i_D^*\, 2\, sinh\left(\frac{F}{2RT}\eta_{tpb}\right)$$

Material and operating parameters are in i_D^* : [1]

$$i_D^* = i_{0,Cr_2O_3,init}\, x_{CrO_2(OH)_2}^{0.5}\, x_{H_2O}^{0.5}$$

METHODOLOGY

1. *Run galvanostatic ERMINE simulation to find local η_{tpb}*
2. *Using η_{tpb} from t_{n-1} and Δt, active tpb at t_n :*

$$V_{act}(t_n) = V_{act}(t_{n-1}) \times exp\left(-i_{D,Cr_2O_3}\frac{V_{mol,Cr_2O_3}}{h_{Cr}zF}\Delta t\right)$$

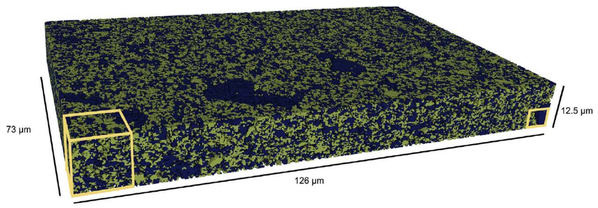
3. *Update the tpb activity for t_n :*

$$S_{0,tpb}(t_n) = S_{0,tpb,init} \times \frac{V_{act}(t_n)}{V_{Em}}$$

**. Iterate through time until termination occurs*

F, R = Faraday , Gas constants
T = temperature (800 °C)
$i_{0,Cr_2O_3,init}$ = exchange current for tpb Cr deposition[1]
x_i = molar fraction of i in gas
$V_{Act}(t)$ = active volume of local element at time t
V_{mol,Cr_2O_3} = molar volume of Cr oxide
h_{Cr} = Maximum height of Cr deposition (35 nm)[1]
z = # of electrons transferred during reaction (6)[1]
$S_{0,tpb}(t)$ = volumetric rate of ORR at tpb at time t
$S_{0,tpb,init}$ = vol. exchange current of ORR at tpb
V_{Em} = volume of local element

Experimental Microstructures (COM-0.48)



Initial Microstructures

Dataset	$\bar{a}$ (µm)	Voxel size (nm³)
SYN-0.34	0.62	125
SYN-0.40	0.70	125
SYN-0.50	0.95	125
COM-0.48	0.46	55x55x50

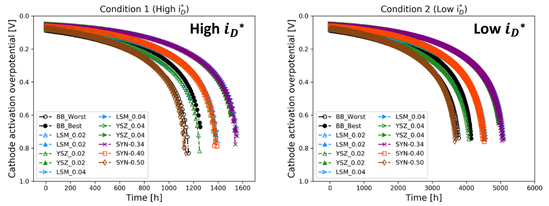
Commercial and synthetic datasets are rescaled to have same average particle size (0.46 um)
Microstructures vary by mean normalized standard deviation in particles size (number in name)
COM-0.46 subvolumes were synthetically infiltrated with different amounts of either LSM or YSZ
Volumes are 10 * 10 * 10 µm³ with bottom 10 * 10 * 3 µm³ portion dense YSZ electrolyte

Galvanostatic Simulation Parameters

Case	i_D^* *(A/cm²)*	*Temperature (°C)*	*Current density (A/cm²)*	$i_{0,Cr_2O_3,init}$ [1] *(A/cm²)*	$x_{Cr\ species}$	x_{H_2O}
High i_D^*	i_D	800	0.2	6.74 x 10^{-4}	3.31 x 10^{-7}	0.026
Low i_D^*	**0.3**i_D	800	0.2	6.74 x 10^{-4}	8.25 x 10^{-7}	0.001

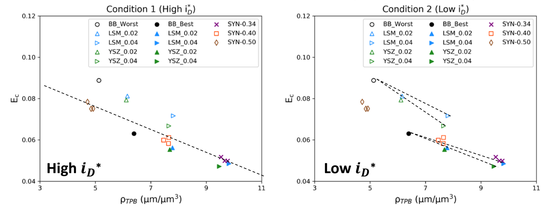
Operating Time and Overpotential in Electrode Microstructures

Cathode Activation Overpotential versus Time



Overall shapes look similar & Lifetime is different.

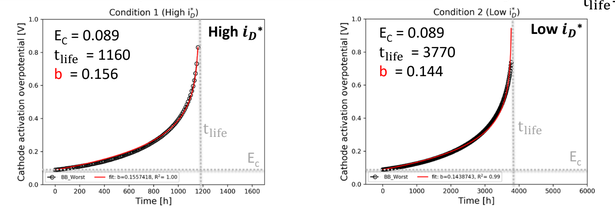
Initial Cathode Activation Overpotential (t =0)



Synthetics linear with tpb ***Infiltrate type affects COM***

Curve Fitting Method

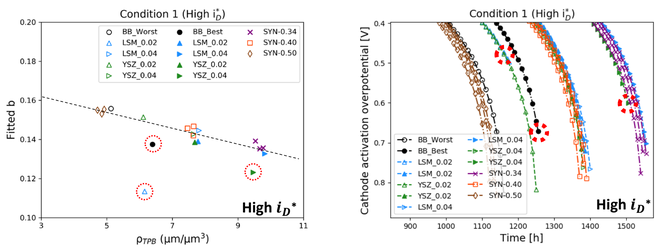
Shapes fit reasonably well to concentration-like curves: $E = E_c + b\ \ln\frac{t_{life}}{t_{life}-t}$



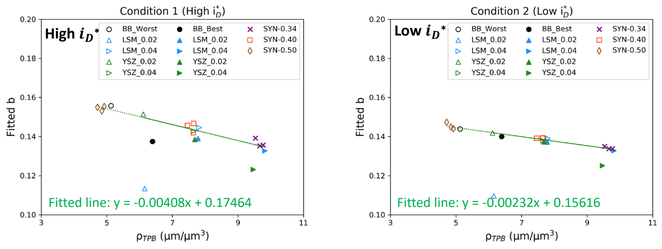
Shapes fit well with b as only fit parameter: E_c and t_{life} from endpoints

Analysis and Predicting Operating Time with Curve Fitting Method

Fitted b value extracted from simulations



b varies with the relative amount of data available (lower with less)



b varies weakly (0.14 ± 0.02) with tpb density, operating conditions, and life

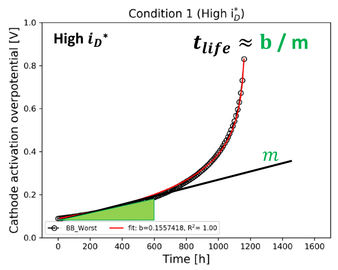
Predicting Lifetime from Initial Data

$$E = E_c + b\ \ln\frac{t_{life}}{t_{life}-t} \approx E_c + \frac{b}{t_{life}}t \approx E_c + mt$$

$$t_{life} \approx \frac{b}{m}$$

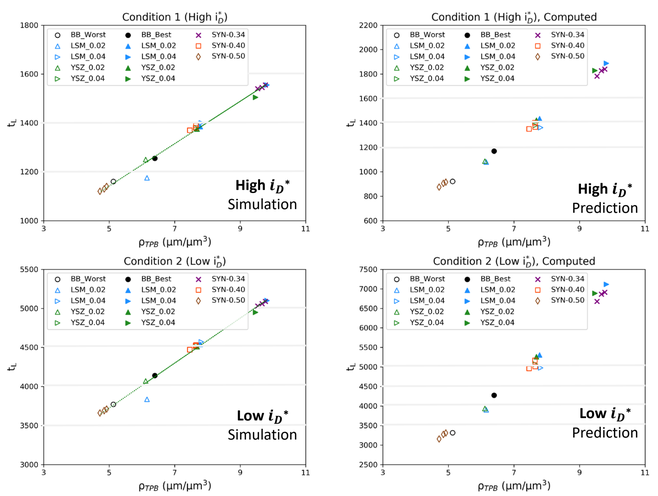
b can be estimated by tpb density and conditions
see images to the left from simulations
m can be determined by fitting early time data
see image below, approximating experiments

We use $0 \le t \le 600$ for High i_D^* cases
We use $0 \le t \le 1500$ for Low i_D^* cases



Can simulations inform experimental predictions?

Simulated versus Predicted Operating Lifetimes



Predictions are within reason, errors < 40 %, increase with lifetime
Most accurate for lifetimes about 2.5 from max of time range.
Simulations can guide and understanding of experimental lifetime!

Conclusions

- Using 19 different microstructures, 2 different operational conditions, and ***thousands*** of individual HPC simulations, Cr-degradation was simulated over long timelines
- High and homogeneous *tpb* densities are essential to suppressing overpotential driven Cr-degradation
- Infiltration increases tpb density, lowers overpotentials, and increases life ≈ 1.33 times on going from to 5 to 10 µm^{-2}
- Cr-degradation decay fits reasonably to progressive decay:
$$E = E_c + b\ \ln\frac{t_{life}}{t_{life}-t} = E_c - b\ \ln\left(1-\frac{t}{t_{life}}\right)$$
- Both t_{life} and b are linear with tpb density when fitted to similar data ranges (time or overpotential)
- Simulations can inform experimental predictions of lifetime
For m = 0.002 V / 1000hr, t_{life} would be 70,000 hr (≈ 8 yr)

Further work is need for different operating conditions and lifetime definitions.