Chemical and Physical Degradation in Solid Oxide Cells: Modeling and Optimization

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Motivation

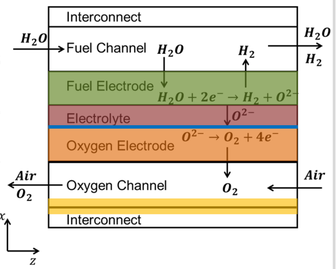
- High temperature operation of solid oxide cells (SOCs) increases their efficiency but accelerates physical and chemical degradation resulting in reduced cell life.
- Non-destructive measurement of time-varying extent of degradation is practically impossible.
- Degradation models are developed for optimal operation and control under electrolysis and power modes.
- Effects of physical and chemical degradation are generally studied independently in the open literature. This study also investigates their synergistic effects.

SOC Degradation Modeling Capabilities

- Chemical degradation is caused by changes in the triple phase boundary (TPB) microstructure due to oxidation, agglomeration and redistribution that in turn affect conductivity, active area, and efficiency.
- Degradation rates are substantially higher under electrolysis due to high oxygen partial pressures in the oxygen electrode.
- Physical degradation is induced by thermal excursion and cycling and causes creep and fatigue damage in cells due to thermal stress evolution.
- Thermal stresses evolve because of time-varying differential thermal expansion between the three layers.

Chemical degradation modeling capabilities

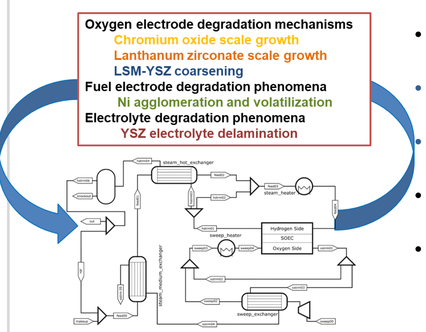
- Dynamic first principles and empirical models include five dominant degradation mechanisms in the three active layers of the SOC.
- Models include parabolic growth laws for oxide growth, Ostwald ripening for Ni agglomeration, and Fick's law for surface diffusion.



Physical degradation modeling capabilities

- Thermal stress models are developed that can capture the effect of time-varying temperature profile within the cell.
- Creep evolution can be calculated, and failure probability analyzed.

Coupling and Solution Methodology



- Degradation models set up as sub-models within SOC model.
- Full discretization over 20k hours of operation is intractable.
- Quasi-steady state assumption for flowsheet level dynamics.
- Model discretized according to degradation dynamics
- Solved fully discretized DAE system as a nonlinear programming problem using ipopt.

Optimization of Long-Term Operation

- Chemical degradation results in changes in the specific energy consumption and thermal performance of the SOC.
- Dynamic optimization of long-term operating conditions is necessary to obtain efficient operation over the lifetime of the system.

Maximize Integral Efficiency over lifetime

$$\max \sum_t \eta_t = \sum_t \frac{HHV(H_2\ produced_t)}{P_{total,t}}$$

Minimize Voltage Degradation Rate

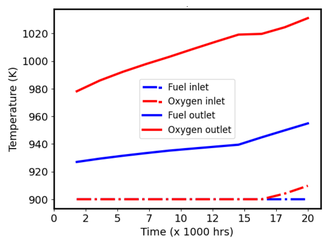
$$\min \frac{\tilde{V}_{tf} - \tilde{V}_0}{\tilde{V}_0}$$

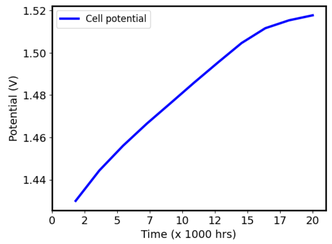
Maximize Lifetime H_2 production

$$\max \sum_t H_2\ produced_t$$

Operating Mode	Objective Function	Specific Energy Consumption (kWh/kg)	Lifetime H2 Production ($\times 10^8\ Kg$)	Voltage Degradation Rate ($\%/\ khr$)
Constant Current Density	Undegraded Cell	35.3	118	None
	Max integral efficiency	36.6	118	2.6
	Min degradation rate	40.4	118	1.8
Constant Potential	Max Integral Efficiency	35.6	88	1.7
	Max lifetime H2 prod.	38.9	100	2.0
	Min final degradation	41.7	40	0.7

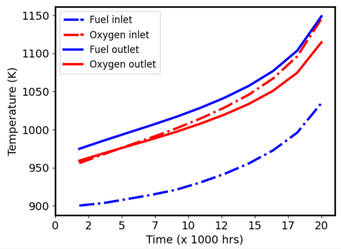
Constant Current Density Operation – Minimize Degradation Rate

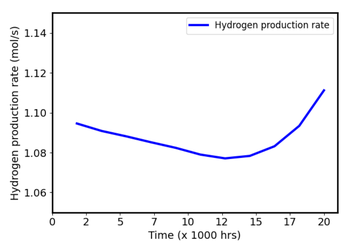




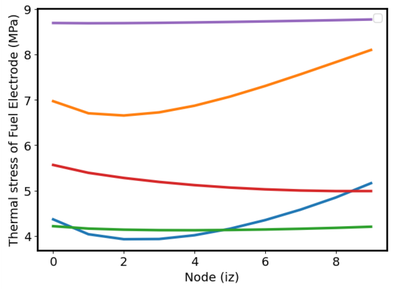
- Constant current density (constant H_2 production rate) operation results in a high degradation rate.
- It is observed that to minimize chemical degradation, it is desired to have low inlet temperatures.
- Tradeoffs between specific energy consumption and degradation rate can be captured depending on the pricing of electricity and hydrogen.

Constant Potential Operation – Maximize Integral Efficiency





Thermal stress characteristics

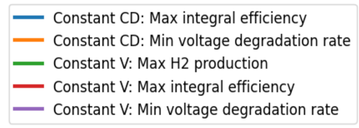


Thermal Stress Profiles after 20,000 hours

- A thermal stress model calculates stresses due to change in the coefficient of thermal expansion.
- Different optimal operating scenarios have different stress distributions.
- Tensile stress in the fuel electrode can result in accelerated failure.
- Optimizing operation to minimize chemical degradation, can result in increased physical degradation.

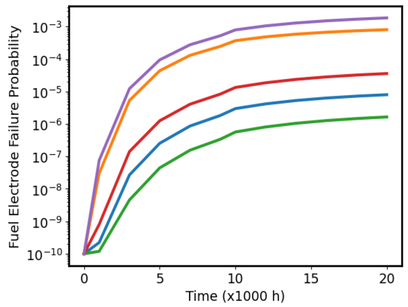
For thermal stress calculations:

- Reference stress free at T_{ref} = 1473 K



Creep Induced Failure Probability

- Extended operation at high thermal stress results in increased creep strain in the SOC.
- The Weibull distribution is used to estimate the failure probability of a given layer.
- The effect of different optimal operating scenarios on failure probability is shown.



- **A tradeoff exists between physical and chemical degradation phenomena.**

Concluding Remarks

- Increased resistance within the cell due to chemical degradation result in higher operating temperatures.
- Time-varying changes in the internal cell temperatures can result in thermal stress buildup.
- Dynamic optimization over lifetime can identify operational strategies to minimize degradation or maintain low specific energy consumption.

Future Work

- Extend degradation models to other leading electrode and electrolyte materials.
- Undertake optimization to minimize LCOH by taking into account operating costs, hydrogen selling price, stack replacement schedule, and stack cost.
- Investigate optimal operating strategies for seasonal H_2 demand.
- Extend thermal stress and creep calculations to sealant layer.
- Develop algorithms for rigorous multi-scale optimization considering both fast and slow time scales over large time horizon.

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