Carbon Resistant High Entropy Alloy Anode for Internal Reforming of Hydrocarbons in SOFC

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Abstract: Solid oxide fuel cells have been recognized as one of the most energy efficient and environmentally clean power generation devices with fuel flexibility. State of the art SOFC's are prone to carbon formation and pulverization of traditional Ni-yttrium stabilized zirconia anode when fueled with hydrocarbons. We present our observations on high entropy alloys (HEA), comprised of multiple low cost non-noble and non-strategic metal alloying constituents that have demonstrated carbon resistance during exposure to methane and alcohol fuels. Demonstrated controllable reforming rates also have potential to benefit homogenization of temperature distribution in cells and stacks. The reformation rate of HEA-Ga doped ceria (GDC) has been measured and compared with that of Ni-Samaria doped ceria (SDC). Carbon resistance has been validated under both external and internal reforming of multiple hydrocarbon fuels. While voluminous filamentary carbon fibers formed on posttest Ni-SDC, no carbon deposition was observed on posttest HEA-GDC anode (scanning electron microscopy and Raman spectroscopy). Electrochemical performance and stability of HEA-GDC‖YSZ‖LSM-YSZ will be presented.

Background: Due to its high operating temperature (600-1000˚C), SOFC power systems have the potential to directly reform a number of hydrocarbon fuel feed stocks (pipe-line natural gas, biofuels, and liquid hydrocarbons) and electrochemically oxidize reformate constituents (H_2, CO) to generate electrical power. For internal reforming operation, SOFCs, however, require anode material that has desired dual catalytic (hetero and electro) properties for controlled reforming and electrochemical oxidation reactions to avoid local cooling or overheating, which can result in mechanical failure due to thermally induced stresses and microstructural degradation. The anode materials also need to remain resistant to carbon formation and pulverization at the cell operating temperatures.

Objective:

- Select anode materials for controlled hydrocarbon reforming to avoid local cooling and overheating.
- Validate select anode materials for direct internal reforming (DIR) at button cell level.
- Scale up the synthesis process, measure cell performance and transfer technology.

Impact:

- Mitigation of carbon deposits in the cell anode
- Improved cell and stack temperature distribution
- Improved cell and stack electrochemical performance and durability.
- Reduced system cost by using DIR solid oxide fuel cells.

Project Plan and Schedule

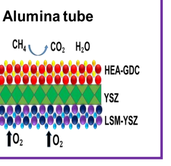
Material selection and synthesis → **Steam/HC reforming** → **SOFC cell validation** → **Technology transfer**

- HEA Alloy models and energetics
- Alloy synthesis by sol-gel and magnetron sputtering
- Demonstrate 1 kg batch process
- Characterization by XRD, BET, SEM-EDS, STEM

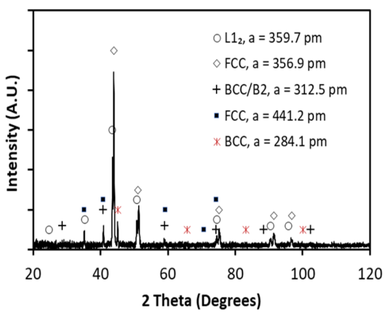
- Bench top validation
- 450-850ºC
- >200 h testing
- Gaseous fuel,CH_4
- Liquid fuel, methanol

- Select optimized materials
- Electrochemical validation
- 1 inch cell anode coating
- 3 cell tests (500-1000 h.)
- Cost/performance model

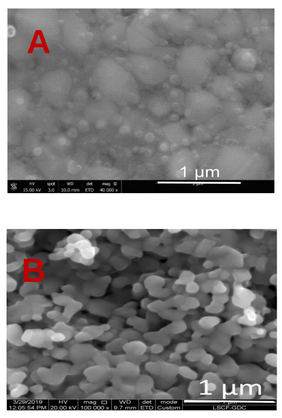
- Identified SOFC industry
- Technology transfer initiated

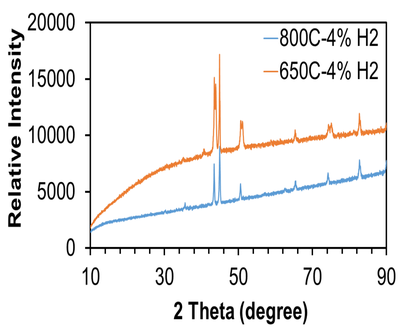


Materials Characterization



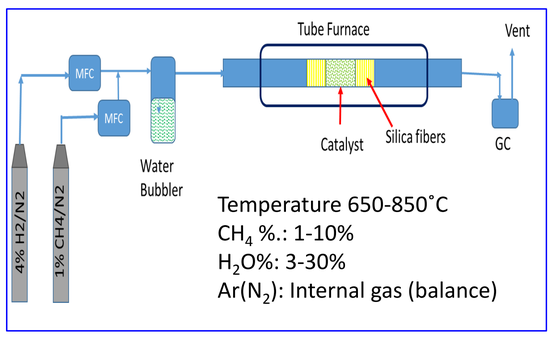
XRD pattern of sputtering coated HEA at UES (A)





XRD patteren of sol-gel HEA At UConn (B)

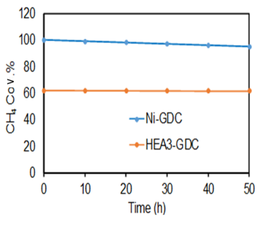
Validation Tests of Select Anode Materials



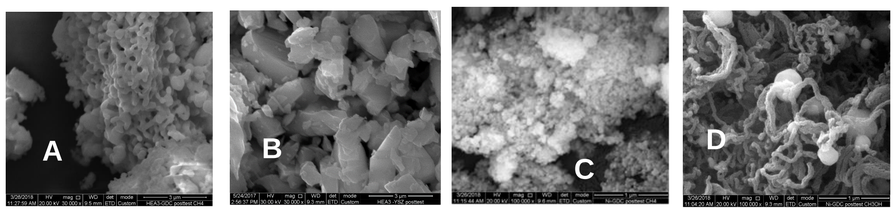
Setup for methane/steam reforming

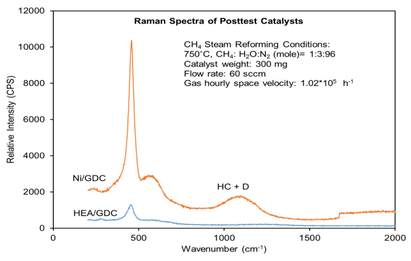
Setup for DIR-SOFC testing using methane fuel

Results – Methane/Steam Reforming



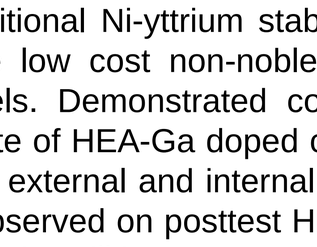
Methane conversion over time in steam reforming reaction at 750˚C. CH_4:H_2O=1:1 (vol.). total flow: 60 sccm, 0.3 g powder.



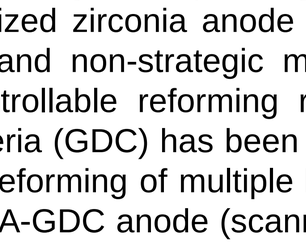


A: Clean posttest HEA/GDC powder
B: clean posttest HEA/YSZ powder
C: Posttest Ni-GDC in CH_4 with carbon deposits
D: Posttest Ni-GDC in methanol with carbon deposits.

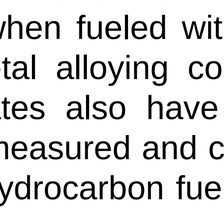
Results of DIR SOFC Cells



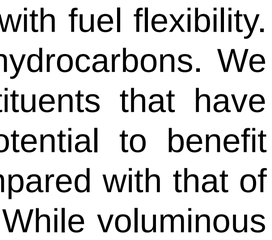
IV and PI curves at 750ºC



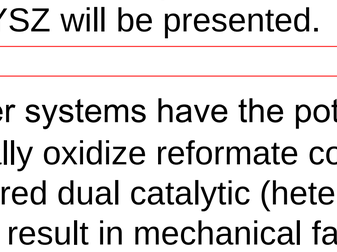
Comparison at Different T.

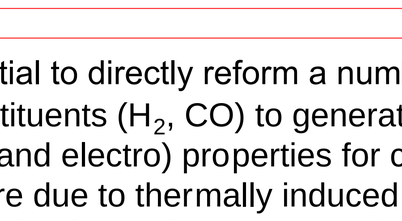


Raman image of posttest HEA-GDC anode

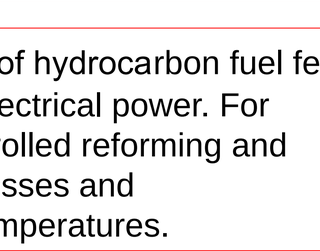


Carbon deposits is not observed on posttest HEA-GDC anode in 10% CH_4/10%H_2O after 100 h at 750˚C.

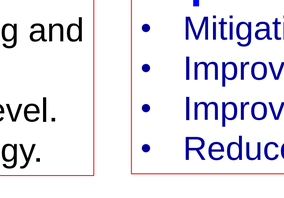


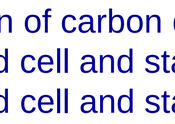


HEA-GDC‖YSZ‖LSM-YSZ,750ºC, 10% CH_4/10% H_2O/N_2

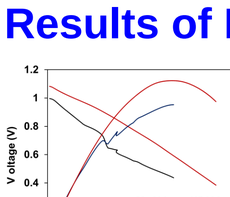


Raman spectra show no carbon deposits on HEA powder.

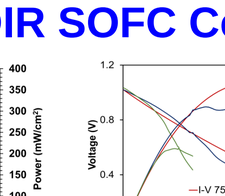




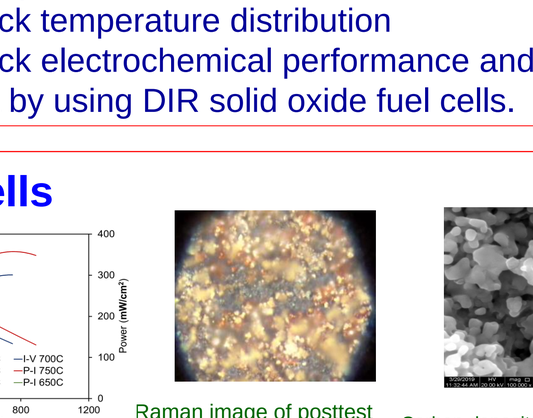
Gas tight button SOFC cells



Pretest anode



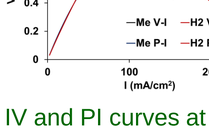
Posttest anode

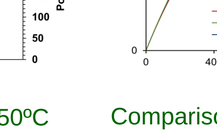


STEM maps of **Pretest** HEA reduced in 4% H_2/N_2 (well dispersed metal elements)

STEM maps of **posttest** HEA in CH_4/H_2O (1:1) (well dispersed metal elements, particle size Change slightly)

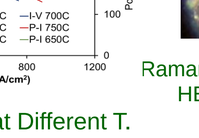
Mechanisms



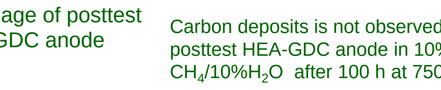


M1-3: transition metals

TEM of pretest HEA



- Transition metal atoms stay near the surface of the Ni matrix. Dopants in alloys lead to dislocations.
- HEA alloys weaken carbon adsorption behavior.
- Carbon gasification dominates at HEA modified nickel surface.



Summary

- As synthesized HEA-GDC anode materials have been validated in steam reforming tests using methane and methanol respectively. Controlled reforming rate over HEA is obtained.
- Direct internal reforming tests have been performed using HEA/GDC‖YSZ‖LSM-YSZ and Ni-GDC‖YSZ‖LSM-YSZ and CH_4 as a fuel at 750-800˚C.
- Both steam reforming tests and DIR electrochemical tests shows that carbon deposition on HEA/GDC is not observed on while carbon deposits on Ni-GDC.
- Characterization data supported the mechanisms of carbon resistance on the HEA anode.
- Our ongoing work focuses on the optimization of HEA formulation to control reforming rate, lower the ASR of the cell, and improve overall electrochemical performance.

References

1. Hu B and Singh P et al., New England Catalysis Society Meeting, MIT, Cambridge, MA, December 7, 2018.
3. Hu B and Singh P et al., Carbon Resistant Electrode for Direct Utilization of Hydrocarbon Fuels in Elevated Temperature Solid State Electrochemical Systems, 49th International Conference on Environmental Systems, 7-11 July 2019, Boston, Massachusetts.

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