UCONN
UNIVERSITY OF CONNECTICUT

UES

Low Cost High Entropy Alloy Anode for Distributed Reforming and Prevention of Carbon Deposition in SOFC

Rabi. S. Bhattacharya, Oleg N. Senkov and A.K. Rai, UES Services Inc., 4401 Dayton-Xenia Road, Dayton, Ohio 45432
Boxun Hu, Junsung Hong, Seraphim Belko, and Prabhakar Singh, University of Connecticut, 44 Weaver Road, Storrs CT 06268

Problem Statement:

There are two issues for Direct Internal Reforming (DIR) on conventional Ni-YSZ cermet anode:

(1) Mismatch between the heat requirement for steam reforming reaction (an endothermic reaction) and the heat available from the oxidation of fuel (exothermic reaction) in the fuel cell section. At SOFC temperatures, the kinetics of the reforming reactions are extremely fast, leading to local sub-cooling around the entrance area of the anode section. However, this can cause mechanical failure because the cooling induces thermal stress in local area.

(2) Carbon deposition on the anode side, which occurs due to the hydrocarbon cracking reaction on Ni. The carbon formation could result in the pulverization of the anode and deactivation of anode material that lead to the loss of fuel cell performance.

Objective:

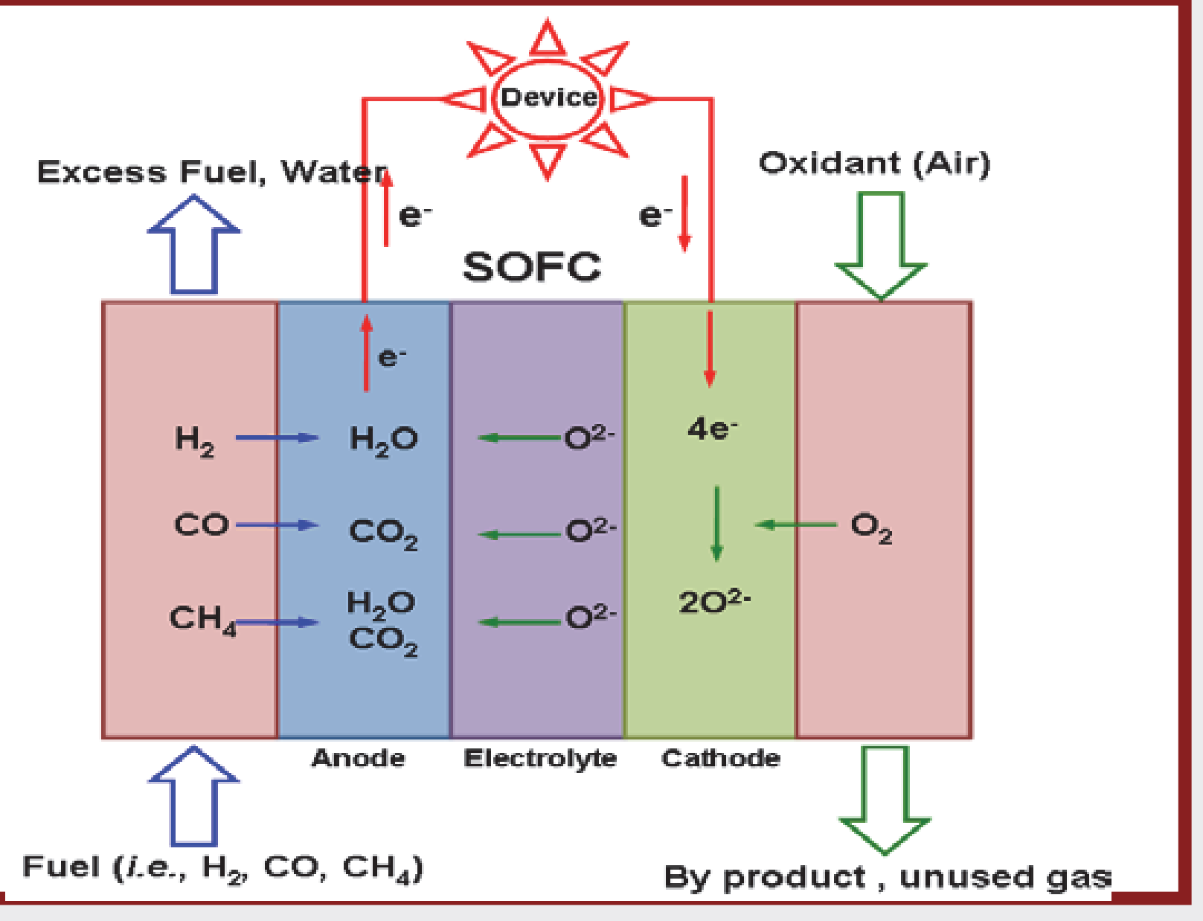
To develop a cost effective alternative anode material for the direct utilization of hydrocarbons in SOFCs that enables distributed reformation over the electrode surface, minimizes temperature distribution in the cell and provides resistance to carbon formation under nominal and transient cell operating conditions.

Background:

SOFC consists of an electrolyte (yttria stabilized zirconia, or YSZ) in intimate contact with a porous anode (Ni-YSZ) and a porous cathode (lanthanum strontium manganite, LSM). The fuel and oxidant gases flow along the surface of the anode and cathode, respectively, and react electrochemically in the three-phase-boundary (TPB) region established at the gas-electrolyte-electrode interface.

Approach:

- To replace Ni in Ni-YSZ cermet with a multi-principal element alloy (MPEA) formed from 3-5 selected elements or high entropy alloys (HEAs), which have at least 5 or more elements.
- The base alloy has significant atom fractions of several elements. A common rationale for this strategy is that the more element number, the higher the configurational entropy, thus improving the stability of disordered solid solution phases.

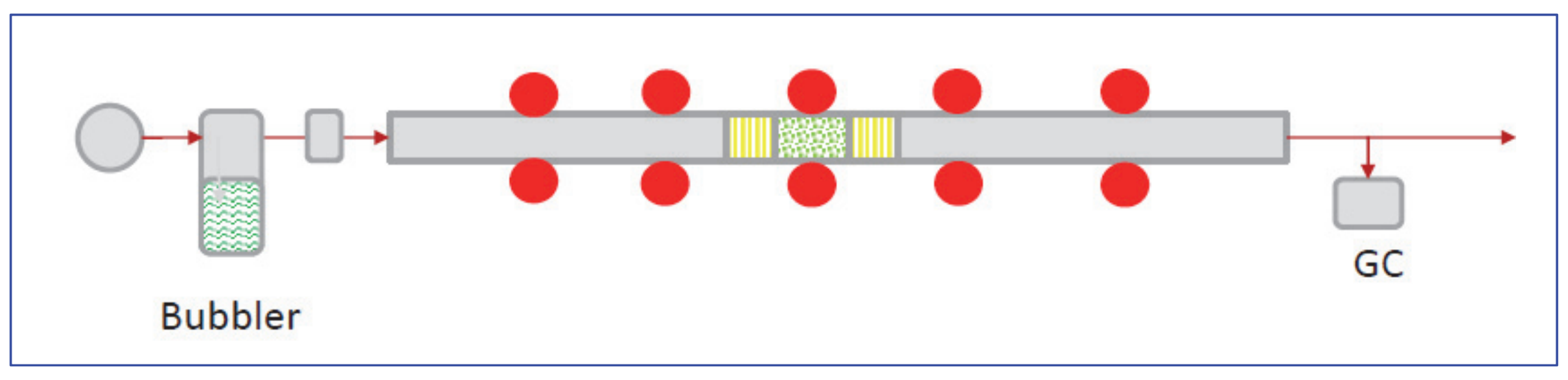


Work Plan:

- Selection of Alloy Composition from Thermodynamic Calculations. All anode formulations will include Cermet chemistry with YSZ.
- Use conventional ceramic and metal powder processing techniques for the synthesis of multi-constituent alloy powder and cermet.
- Prepared anodes will be tested for catalytic activity.
- Fabricate button cells, perform electrical testing of fabricated cells, comparison of performance with base line cell (I-t) and performance analysis (electrode polarization, gas analysis, and structural changes).

Work Performed:

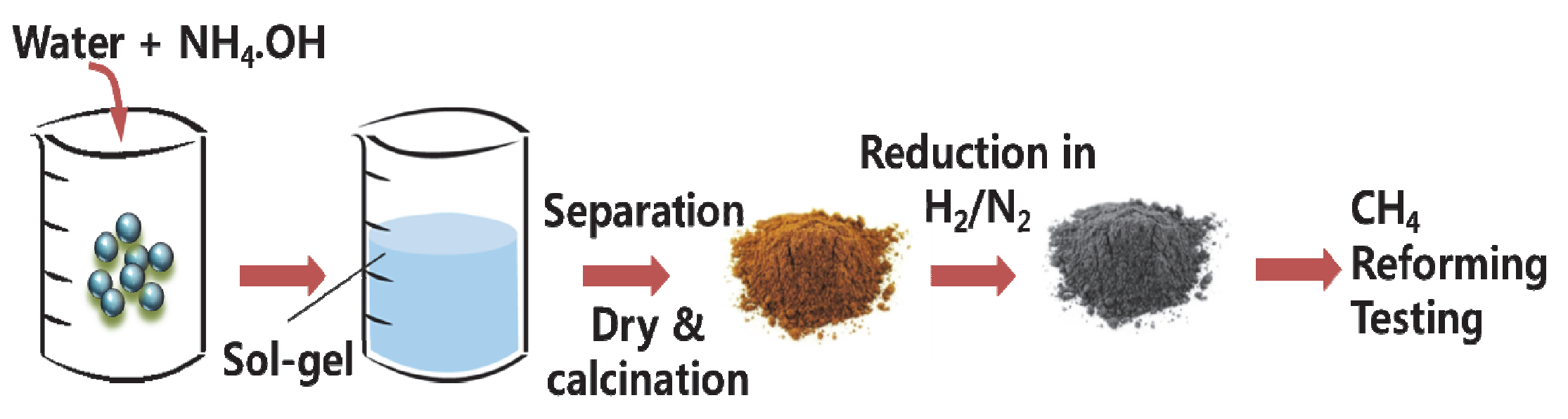
- Performed thermodynamic modeling to guide alloy development using 3-5 selected elements. To ensure microstructure stability, the selected compositions were free from first-order phase transformations at temperatures up to 950 °C.
- Selected 3 alloys of 3, 4 and 5 elements termed HEA1, HEA2 and HEA3 respectively.
- Used sol-gel and co-precipitation techniques to synthesize alloy powders.
- Characterized powders for morphology and composition using SEM/EDS and XRD.
- Bench top reformation study was conducted to compare the reformation rate of CH_4-H_2O using HEA and Ni-cermets.
- Carbon formation was studied by SEM/EDS and Raman spectroscopy.



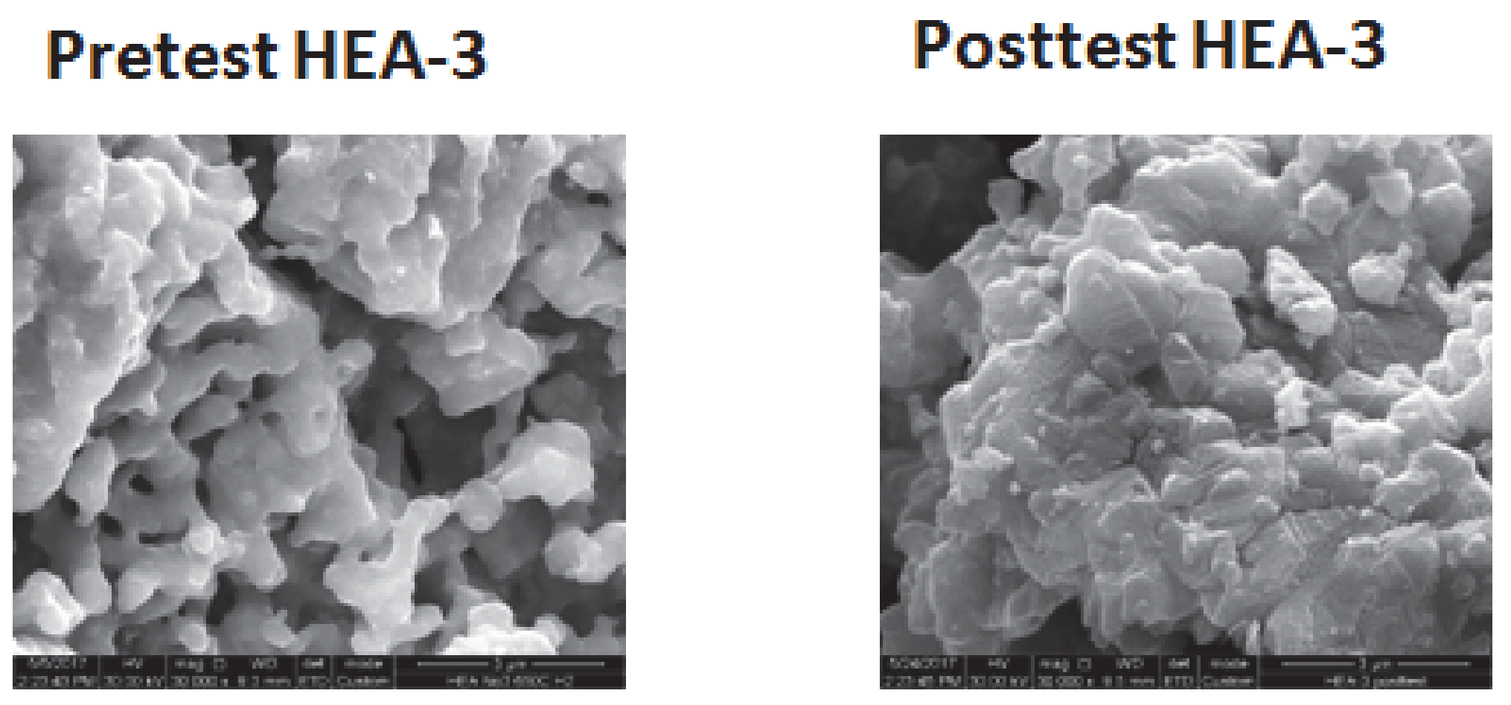
[Schematic diagram for reforming efficiency test]

Results & Discussion

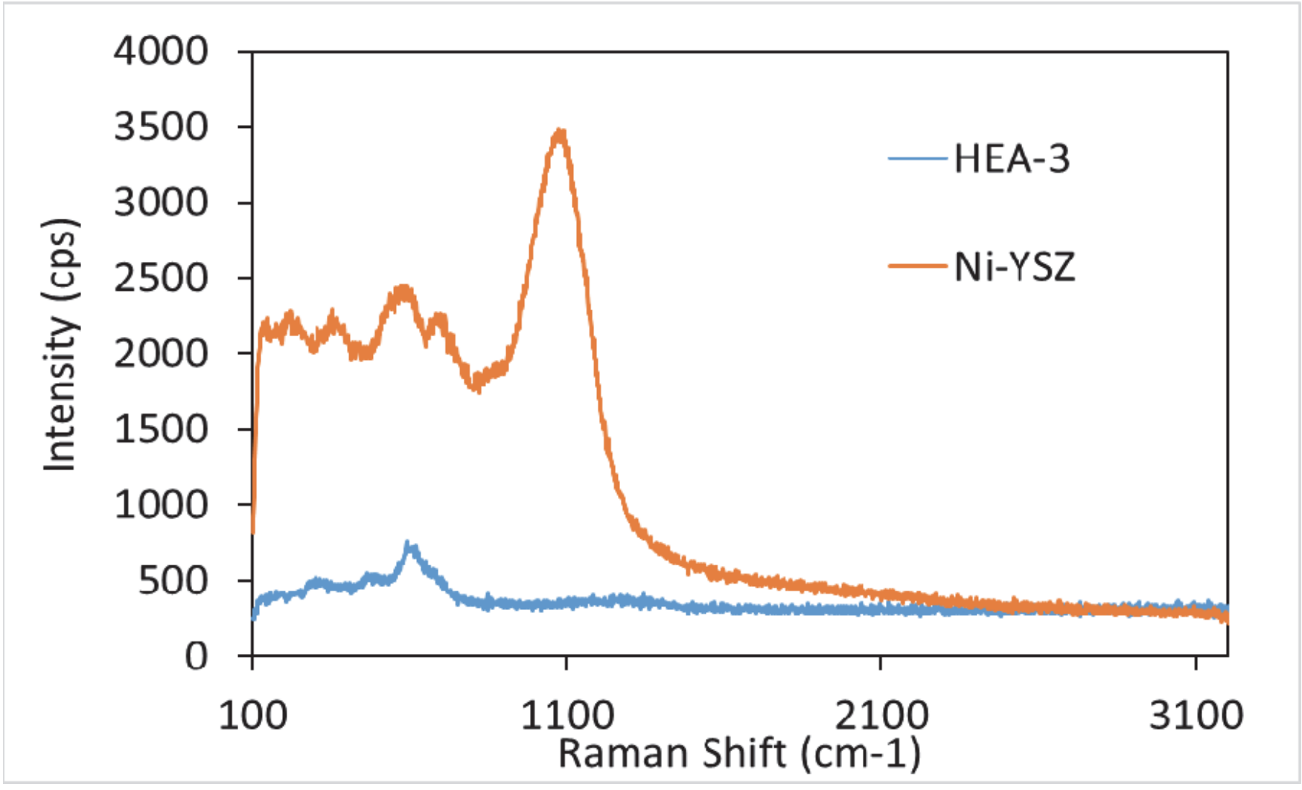
Flow Chart for HEA power synthesis



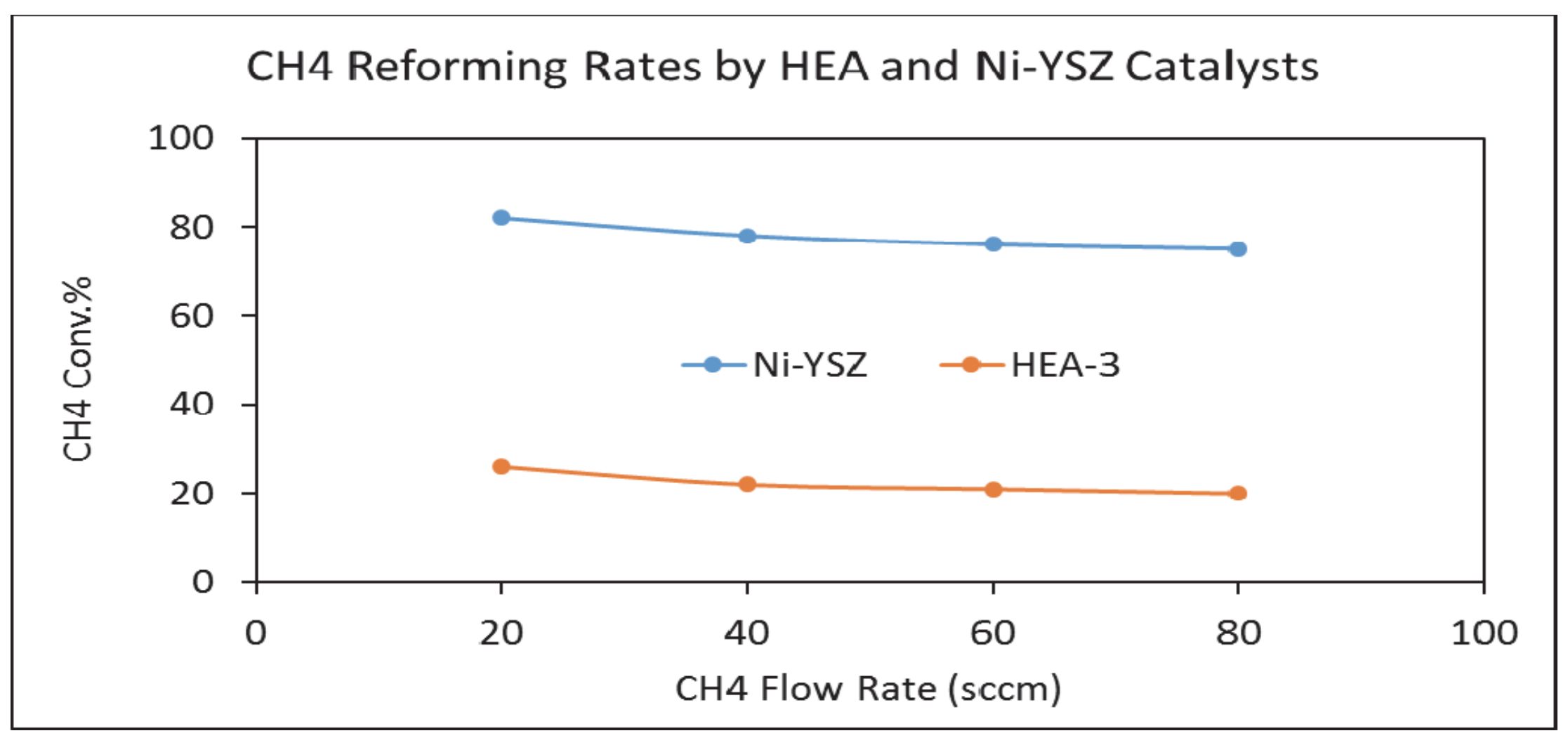
- Green sol-gel synthesis method at low temperature
- Use of low cost, non-toxic, non precious materials
- Rational selection of alloy compositions from thermodynamic calculations.



Postreaction metal powder maintains microstructure stability. No carbon formation was observed.



Raman spectra shows only HEA and YSZ relevant peaks. No carbon peaks present on HEA powders.



HEA power shows less reforming rate compared to Ni-YSZ at 750 °C using 1% CH_4 / 3%H_2O / N_2.

Summary:

1.Experiments have demonstrated that the CH_4 reforming rate can be controlled by as-proposed HEA alloy catalysts and its reforming rate is slower than that of Ni-YSZ powder at 750°C.
2.The microstructure of the designed HEA catalysts are stable and no carbon formation was observed in post-test HEA-3 by SEM-EDS and Raman spectroscopy.
3. HEA chemistry will be further optimized and powder will be synthesized using low cost wet chemistry techniques.
4. As-synthesized HEA catalysts will be tested for hydrocarbon reformation as well as anode in electrochemical cell.

References:

1.Tsai, Ming-Hung, and Jien-Wei Yeh. "High-entropy alloys: a critical review." *Mater. Res. Lett.* 2.3 (2014): 107-123.
2.Pakhare, Devendra, and James Spivey. "A review of dry (CO_2) reforming of methane over noble metal catalysts." *Chem. Soc. Rev.* 43.22 (2014): 7813-7837.
3.Bimbela, F., et al. "Ni/Al coprecipitated catalysts modified with magnesium and copper for the catalytic steam reforming of model compounds from biomass pyrolysis liquids." *Appl. Catal. B: Environmental* 119 (2012): 1-12.
4.Resini, Carlo, and Michele Sisani. "Nickel versus cobalt catalysts for hydrogen production by ethanol steam reforming: Ni-Co-Zn-Al catalysts from hydrotalcite-like precursors." *Inter. J. Hydrogen Energy* 35. (2010): 5356-5366.

Acknowledgement: Funded by DOE STTR Phase I, DE-SC0017050, DOE Program Manager, Jason Lewis