Carbon-free and Electrochemically Active High-Entropy Alloy (HEA) Anode for SOFC Applications

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Abstract: Internal reforming of hydrocarbon fuels (pipe line natural gas) in solid oxide fuel cells (SOFCs) is primarily limited by cooling at the cell inlet and carbon formation on the nickel base anode. An alternate anode chemistry comprising of high-entropy alloy (HEA) containing Cu, Ni, Co, Fe and Mn has been synthesized using the co-precipitation method and experimentally evaluated for reforming and electrochemical activity under standard SOFC operating conditions. HEA anode/ catalysts were analyzed including SEM, XRD, TPR, TPO and TPD. Compared with standard Ni/YSZ and Ni/GDC anodes, HEA containing gadolinium-doped ceria (GDC) showed controlled and distributed reforming of methane. Unlike nickel base anode that showed the formation of filamentary carbon, analysis of HEA/GDC anode by Raman and SEM microscopy showed absence of carbon.

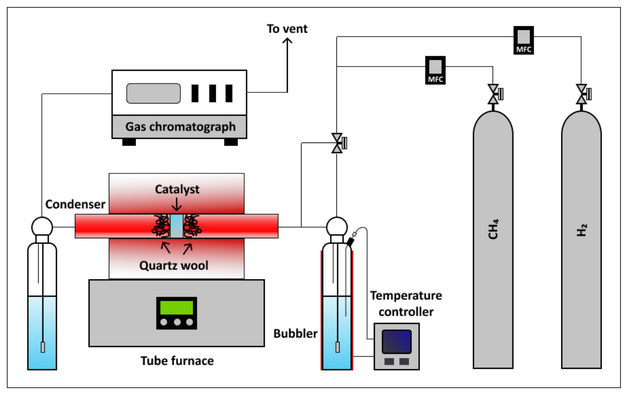
Objective:
- Develop advanced anode / catalyst that prevents filamentary carbon deposition during internal reforming of methane in SOFC
- Develop advanced anode that reduces endothermic cooling at the cell inlet under internal reforming mode without compromising electrochemical activity of the cell

Accomplishments:
- Carbon-free cell operation
- Distributed reforming
- Comparable cell performance
- Lower cost and conventional materials

Background: Since SOFCs operate at high temperatures (600-1000 ˚C), there has been a need for developing electronically conductive and electrocatalytically active anode material for direct reforming hydrocarbon fuels on the anode, followed by simultaneous electrochemical oxidation of produced H2 to generate electricity. Conventional SOFCs utilize standard Ni/YSZ, which has shown to suffer from excessive cooling and coke formation due to extremely high surface reaction. In this work, a novel anode material known as HEA is carefully synthesized and optimized for controlled hydrocarbon reforming and electrochemical oxidation reactions, without mechanical failure and carbon formation.

Experimental Setup and Conditions:

Bench-top experiment:

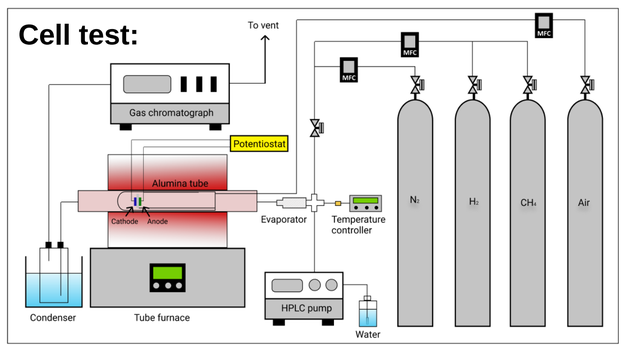


Temp: 700 – 800 ˚C
GHSV: 45 000 h^{-1}
S/C ratio: 2

Steam reforming of CH_4:
$CH_4 + H_2O \rightarrow CO + H_2$

Coke pathway:
$CH_4 \rightarrow C + 2H_2$
$2CO \rightarrow 2C + O_2$

Cell test:



Temp: 750 ˚C
Cathode: 150 CC of air
Anode: 100 CC of 10% $CH_4 + H_2O + N_2$ (bal)

Oxidation of H_2:
$2H_2 + 2O^{2-} \rightarrow 4e^- + 2H_2O$
Reduction of O_2:
$O_2 + 4e^- \rightarrow 2O^{-2}$

HEA Anode Materials and Cell Configuration:

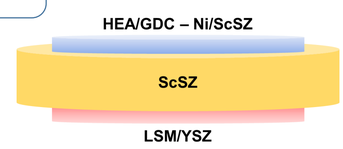
Computation analysis ⇔ Selection of HEA anode materials ⇔ Thermodynamic prediction of carbon formation

Heat metal nitrates in DI water → Add citric acid as chelating agent → Add ammonium hydroxide → Precipitate metal hydroxides → Calcine

Deposit Ni/Sc/Sz function layer → Deposit LSM/YSZ on cathode side → Screen-print HEA/GDC on functional layer → Sinter

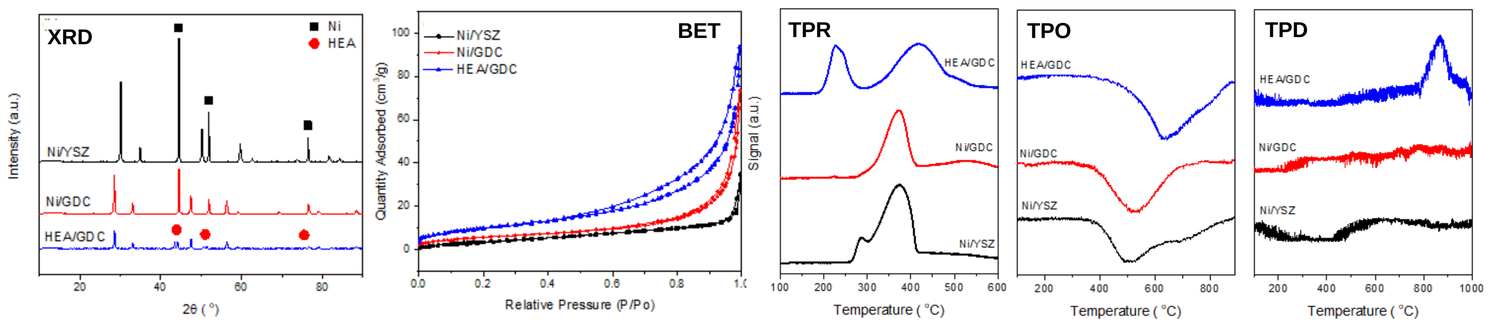
Optimized formulation:

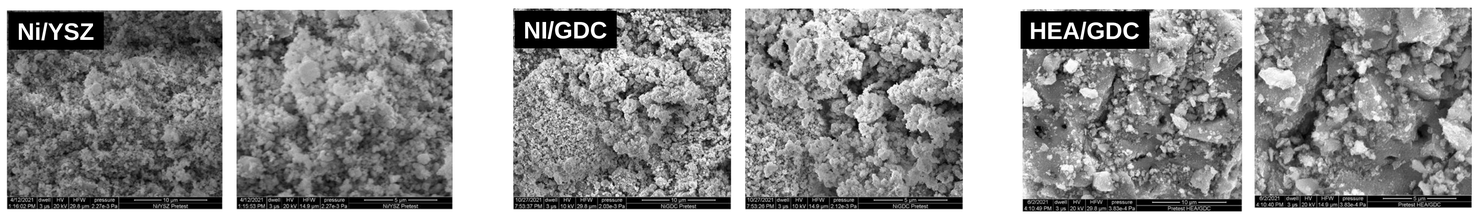
Metal	Wt%
Ni	15
Co	20
Cu	25
Fe	25
Mn	15



Materials Characterization:

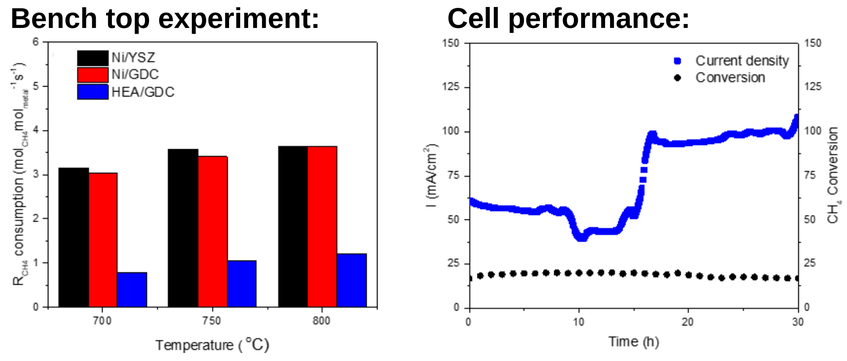
Catalyst	S_{BET} (m^2/g)	Pore volume (cm^3/g)	H_2 adsorbed ($\mu mol\ H_2/m^2$)	O_2 desorbed ($\mu mol\ O_2/m^2$)	TPD ($\mu mol\ O_2/m^2$)	Metal loading (wt %)	Metal dispersion (%)	Crystal size (nM)
Ni/YSZ	15.2	0.043	475.6	15.5	0	45.2	0.327	310
Ni/GDC	21.3	0.101	304.1	16.7	0	43.2	0.220	461
HEA/GDC	35.0	0.129	312.4	22.6	1.2	50.4	0.203	517





Methane Reforming and Electrochemical Test:

Bench top experiment:

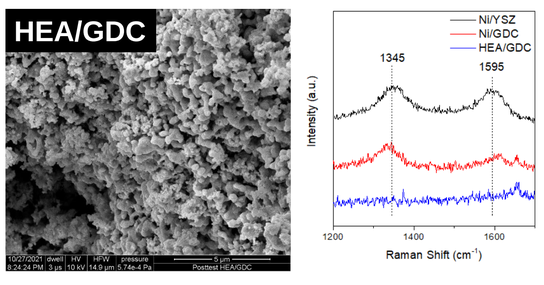


Cell performance:

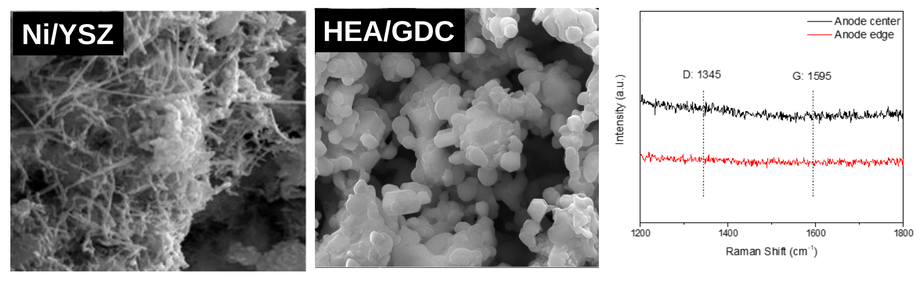
Ni/YSZ and Ni/GDC show high endothermic reaction rate. HEA/GDC showed lower conversion rate of methane. H_2 yield of Ni/YSZ and Ni/GDC are slightly higher than HEA/GDC. After 30 h of TOS, HEA/GDC remains stable at ~20% conversion. Current density remains stable at ~100 mA/cm^2 after 15 h. Overall non-ohmic resistance decreases and ohmic resistance remains stable.

Posttest Characterization by SEM and Raman:

Bench top experiment:



Cell test:



No sign of amorphous or graphitic carbon on HEA/GDC. After cell test, carbon deposits are observed on Ni/YSZ.

Summary:
- HEA/ anode / catalyst exhibits moderate reforming rate for distributed reforming and excellent coking resistance
- Moderate reforming rate is important for maintaining controlled temperature distribution and current density
- HEA/GDC is a promising low cost anode candidate for direct utilization of hydrocarbon fuels in SOFC

Implementation:
- Operating SOFC with hydrocarbons offers infrastructure and commercialization benefits
- Scale-up and long-term stability of electrode performance under SOFC operating conditions need further study

Reference:
1. K. Lee and P. Singh et al. *Intl. J. Hydrog. Energy* 2022
2. M. Tucker and P. Singh et al. *Intl. J. Hydrog. Energy* 2022
3. R. Bhattacharya and P. Singh et al. *US Patent US20220246947A1* 2022
4. B. Koeppl and N. Karri, *PNNL Report*, 2020

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