Carbon-Based SOFC Power System in China

Min-Fang Han
Tsinghua University
Department of Thermal Engineering
State Key Laboratory of Power Systems

Chinese Fuel Cell Committee, Vice Chairman & Secretary-general
Chinese Solid State Ion Committee, Vice Chairman
Technical Committee for Standardization of High Temp. Fuel Cell, Director
Contents

◆ SOFC Target in China
◆ SOFC Technical Development
◆ SOFC Industrialization
Coal Based Energy System in China

- **Background:** Coal is the main energy source in China
  研究背景：化石资源是人类的主要能源来源，中国以煤炭为主要能源，仍然是我国的基础能源

- **National demand:** Efficiency and Environmental Protection
  国家重大需求：提高煤炭利用效率，降低煤炭用量，减少环境污染

- **Solution:** New power generation technology----Carbon-based SOFC power generation system
  解决方案：寻求新的发电技术——碳基燃料固体氧化物燃料电池(SOFC)发电系统

**Carbon-based fuel:**

- **Gaseous:** Natural gas, coal gas, coal-bed methane, biomass gas
- **Liquid:** Gasoline, diesel and alcohols
- **Solid:** Coal
SOFC Teams—Research Map in China

- 60+ universities, institutes and companies
- 1000+ researchers in SOFC related works
Funding Supports for SOFC in China

◆ **NSFC**: National Natural Science Foundation of China

◆ **MOST**: Ministry of Science and Technology
  - National Basic Research Program of China (*973 Program*)
  - National High-tech R&D Program (*863 Program*)

◆ **MOE**: Ministry of Education

◆ **CAS**: Chinese Academy of Sciences

◆ Provinces, Local Government and Others

◆ Industries, Banking and Venture capital (VC)

◆ **MIIT**: Ministry of Industry and Information Technology

◆ **NDRC**: National Development and Reform Commission

◆ **NEA**: National Energy Administration
NSFC Supports for SOFC

- During 2002-2015, more than 140 projects were supported by the NSFC, with about ¥60 million in grants.
- In the National Medium-Long-Term Program for Science and Technology Development (2006-2020), the SOFC is set as one of the most important technologies for distributive energy supply.

- New materials
- New designs
- New theories
- New methods

Cumulative number and fund of NSFC program related to SOFC from 2002 to 2015
MOST Programs for SOFC

In the last 12th “Five-Year Plan”:

◆ 863 Program: Key Technologies of Fuel Cells and Distributed Power Generation System, 2011-2014, 80 M. CNY

◆ 973 Program: Fundamental Research on Carbon-Based SOFC System, 2012-2016, 34 M. CNY
### Key Technologies of Fuel Cells and Distributed Power Generation System

**2011-2014, 80 M. CNY**

<table>
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<th>TASK</th>
<th>RESPONSIBLE</th>
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<td>1 Fuel Cell technology Integrated Natural Gas Reforming to H₂</td>
<td>DICP</td>
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<td>2 1 kW AAEMFC (Alkaline Anion Exchange Membrane FC)</td>
<td>DICP</td>
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Fundamental Research on Carbon-Based SOFC System

2012-2016, 34 M. CNY

Team Member:

- China University of Mining and Technology, Beijing
- University of Science and Technology of China
- Institute of Physics, CAS
- Shanghai Institute of Ceramics, CAS
- Tsinghua University
- Harbin Institute of Technology
- Shanghai Jiao Tong University
- University of Science and Technology Beijing
- Institute of Chemical Defense
- Hua Tsing Power Sci & Tech Co., Ltd.

Chief Scientist: Prof. Minfang Han
13th “Five-Year Plan” Program——from MOST

Coal Gasification Power System Combined CO₂ Near Zero Emission
CO₂近零排放的煤气化发电技术
2017-2021，30+96=126 M CNY
Clear Coal Technology

Team Members:
Huaneng Group
Tsinghua University
Hua Tsing Power Sci & Tech Co., Ltd.
China University of Mining and Technology, Beijing
Shenhua Group

Chief Scientist: Prof. Suping Peng
**Coal Gasification Power System Combined CO₂ Near-zero Emission**

**Objectives**
- Mechanism, system design, and key equipment manufacturing technology of Integrated Gasification Fuel Cell (IGFC) power generation
- The MW-scale CO₂ near-zero emission IGFC demonstration system
- Schematic design and technological packages for 100 MW-scale CO₂ near-zero emission IGFC system

**Key scientific issues**
- The carbon transport pathway and energy conversion mechanism in IGFC system
- The key equipment, reaction and pollutant generation rules in IGFC system
- Synergistic reaction mechanism of CO₂ capture and energy conversion process

**Desired achievements**
1) 100kW class H-T fuel cell power generation with efficiency ≥ 50%
2) Demonstration of MW-scale IGFC system with CO₂ capture ≥91%
3) Schematic design and technological packages for 100 MW-scale IGFC system, with CO₂ capture ≥91% and power generation efficiency ≥47%
SOFC Target 2025~2030 in China

《Made in China 2025》
Energy equipment implementation plan, (NDRC, MIIT and NEA, 2016.6.22)
9. Fuel cells
——Hundreds KW to MW SOFC-based distributed power generation system:
Key technologies: catalytic materials, membrane and electrode, high-temperature interconnector; lifetime over 40000 h; Mass production and system integration

《Energy Revolution Innovation Plan (2016-2030)》
➤ Strategic Direction: Fuel cells for distributed generation
Focus on research and development of PEMFC, SOFC, MeAFC as well as the design and system integration of distributed hydrogen production with fuel cells.
➤ Innovation target by 2030
Service life of SOFC distributed power generation over 40000 h.
➤ Innovation action: SOFC-based distributed power generation
Demonstration of Hundreds KW to MW level SOFC-based distributed power generation system with efficiency over 60; Developing distributed power station for remote cities and industrial enterprises.

NDRC——National Development and Reform Commission
MIIT——Ministry of Industry and Information Technology
NEA——National Energy Administration
SOFC roadmap (2016-2030)

Hydrogen and Fuel Cell Technology Innovation:
——Fuel cell based distributed power generation

For SOFC Target

- Teams
- Technical development
- Industrial breakthrough
- Policy support

- Application of 100kw PEMFC power generation system with service life over 10000 h;
- Demonstration of 100kw to MW SOFC power generation system with service life over 40000 h and electrical efficiency over 60%;
- Demonstration or scale application of MeAFC power generation system with service life over 10000 h.

2016 2020 2025 2030 2050

- SOFC
- MeAFC
- PEMFC

Legend:
- Technical research
- Demonstration
- Application promotion
How to do for SOFC in China?

- 2016.11, Chinese Fuel Cell Committee
- 2017.03, Technical Committee for Standardization of H-T Fuel Cell

To Start the technical standards of SOFC system
To set up SOFC Standard test center:
AQSIQ + Tsinghua University + Local Government

The SOFC roadmap in details?
Contents

◆ SOFC Target in China
◆ SOFC Technical Development
◆ SOFC Industrialization
Fundamental Research on Carbon-Based SOFC System

1. Carbon-based Fuel
   - Anode reaction characteristics
   - Ni-YSZ cermet anode modification
   - Novel perovskite Coking-resistant & Sulfur-tolerant anode materials

2. Interface Stability issues
   - Based on the “porous | dense | porous” tri-layer structure design
   - Tri-layer structure theoretical foundation
   - High performance and stability

3. Conduction mechanism and theoretical system
   - Electrons and ion transport mechanisms in multiphase system
   - Evolution of SOFC multiphase interface
   - From Powder To Power
Carbon-based Fuel in SOFC

- **Thermodynamics of carbon deposition**
  - Carbon deposition area narrows down at elevated temperature

- **Dynamic mechanism of carbon deposition resistance**
  - Carbon deposition rate can be reduced by adjusting the parameters of $P$, $T$.
  - Coking kinetics of CH$_4$ on Ni under non-isothermal conditions

- Carbon deposition can be reduced or even removed through adjusting gas composition.
Ni-YSZ Cermet Anode Modification

Influence factors of coke resistance on catalyst surface: structure and acidity

1. Particle size and dispersion of Ni
2. Acidity of supports
3. Interaction between Ni and supports

The high activity and stability can be maintained by loading MO (M=Mg, Ba, Sn) on Ni-YSZ anode with CH₄.

Dislocations (see arrows) are introduced to relax the strain resulted from the decomposition of Ni₃C in NiMgO.

Ni₃C is an intermediate phase during carbon deposition process.

2.5wt% MgO coated NiO, MgO modified Ni show good coke resistance.

H₂O easily dissociated on MgO, forming COH with the deposited carbon.

COH dissociated on Ni surface, forming CO, and then oxidized into CO₂ by O radical.
Anti-carbon deposition by load of nano-SDC
电极上负载纳米SDC改性具有普适性
在阳极上负载SDC，提高甲烷气氛下催化活性和稳定性

- Anti-carbon deposition can be achieved by in-situ loading of nano-metal oxide
  原位负载金属氧化物（BaO/MgO/SDC）可以改善抗积碳性能

- Stable operation of the SOFCs in methane was achieved after in situ loading of SDC
  原位负载SDC提高了阳极在甲烷中的催化活性，实现了电池在甲烷中的稳定运行

Loading of SDC in the anode inhibit the formation of nickel carbide

**Anti-carbon deposition mechanism:**

The loading of nano SDC effectively inhibits the formation of nickel carbide.

Little nickel carbide is found, the particle size remarkably decreases (2-5 nm).
Novel Perovskite Anode Materials

Anode with perovskite structure is coke resistance, sulfur tolerant and renewable

- La$_{0.4}$Sr$_{0.6}$Co$_{0.2}$Fe$_{0.7}$Nb$_{0.1}$O$_{3-\delta}$ (LSCFN)

- LaNi$_{0.6}$Fe$_{0.4}$O$_{3-\delta}$ (LNF)

- Directly hydrocarbon fueled
- In-situ precipitated Nano Co-Fe particle.

- Excellent stability under hydrocarbon fuel
- Excellent redox cycling stability

- Nano alloy particles enhanced the electronic conductivity and fuel catalytic activity.

Tri-layer Structure Design

— Higher stable performance with continuous interface

Normal issues in sandwich-structure

Crack, peeling off and incompatibility etc..

Design and fabrication of tri-layer cell

Cathode

Electrolyte

Anode

Design — Tri-layer structure: Eliminate the interfacial problems, improving the long-term stability of SOFC.

Tri-layer structure:

Porous cathode support || densified electrolyte || porous anode support

Porous cathode support || densified electrolyte || porous anode support

Tri-layer (High stable matrix)

Co-press

Co-sinter

Tri-layer structure: Eliminate the interfacial problems, improving the long-term stability of SOFC.
TBP is the main place of electrode reaction, structural design of electrode is essential.

- In situ loading of nano-electrode can significantly improve the TBP length and reduce electrode polarization resistance, laying the theoretical foundation for the high-performance.

\[ L_{\text{eff}} = \frac{(2r_{\text{io}}A)}{p}, \quad \text{cm cm}^{-3} \]

\[ R_p, \quad \Omega \text{cm}^2 \]

\[ p=1, \text{ composite}; \quad p=0.1, \text{ infiltrated}; \quad p=0.02, \text{ infiltrated} \]

\[ r_{\text{io}}, \mu m \]

\[ L_{\text{eff}} \text{ vs. } r_{\text{io}}, \mu m \]

\[ R_p \text{ vs. } r_{\text{io}}, \mu m \]

Optimization of In-situ Loading Nano-cathode Materials

- **In situ loading of** $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF)

  - Infiltrated LSCF layer with thickness of ~2μm
  - Nano particle of LSCF
  - No extra phase formed between LSCF and YSZ interface

- **Performance of NiO-YSZ/ YSZ/YSZ tri-layer cell infiltrated with LSCF**

  **Achievements:**
  - Uniform loading ;
  - Optimal loading amount of 45wt.%.

In-situ loading technology applied to 10cm × 10cm tri-layer SOFCs

Achievements:

- 10cm × 10cm tri-layer SOFCs using in-situ loading technology

- Pilot production with stable preparation process
Third-party Evaluation of 10cm×10cm Tri-layer SOFCs

High performance under hydrogen and (simulated) methane reforming gas was validated by DTU.

测试结果表明，在氢气及（模拟）甲烷重整气下表现出高的性能
10cm × 10cm tri-layer SOFCs show high output performance and good stability.

- **Third-party evaluation:** Technical University of Denmark, Risø Laboratory;
- **Stable operation at 750°C.**
Electrons and Ion Transport Mechanisms in Multiphase System

1 Oxygen reduction process at Cathode TBP
- Develop ECR theory, determine the reaction rate constant at TBP.
- Quantify the contribution of TPB, determine the polarization resistivity at TBP.

2 Ion transport at interface between electrode and electrolyte
- Cerium oxide intermediate layer \( R_p \propto \sigma^{l} P_{O_2}^{n} \)

3 Anodizing process at TBP
- Determine the reaction rate constant at anode TBP
- Quantify the contribution of TPB to anode reaction process

Microstructure Performance

Quantification

Reaction action energy lower to 0.836 eV from 2.399 eV at TBP

The linear relationship of polarization resistance \( R_p \) of LSCF to \( ln\sigma \)
Formation and Evolution of Multiphase Interface

1. Formation and evolution of 2PB, 3PB in composite electrode
   - Propose the kMC and analytical sintering model for composite electrode
   - Predict the formation of 3PB and 2PB

2. Formation of multiphase interface (2PB, 3PB) in electrode with tri-layer structure
   - Theoretical model for integration microstructural electrode

3. Mechanical stability of multiphase interface under electric field

SOFC Theoretical System
——From Powder To Power

Performance

Scientific issues

1. 3PB reaction kinetics;
2. Electron and ion transport in electrode;
3. Ion transport in electrode and electrolyte interface;
4. Flow model in film electrode.

Construction of high-performance electrode and its electrochemical behavior

1. Formation and evolution of 2PB and 3PB;
2. 2PB and 3PB in tri-layer SOFC electrode;
3. Stability under electric field;
4. Mechanical model of thermal cycling.

Microstructure

Electron and ion transport mechanism in multiphase system

Evolution of multiphase interface

DFT calculations
Intrinsic properties
Microstructure
Simulation

Performance of single cell
Performance of stack

$m$
$10^{-9}$ $10^{-6}$ $10^{-3}$ $10^{0}$

Powder

3PB
2PB

Structure stability

Preparation

Heat treatment

Heat treatment

Heat treatment

Heat treatment

Heat treatment

Heat treatment

Power

Performance
Contents

◆ SOFC Target in China
◆ SOFC Technical Development
◆ SOFC Industrialization
Progress in SOFC-industry Chain

Materials → Cells → Integration module → System → Users

From powder to power
SOFC Key Materials

**Electrolyte Materials**

- 8YSZ: $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ (GDC)
- 10ScSZ: $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ (SDC)
- 10Sc1CeSZ: $\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_{2-\delta}$ (YDC)
- La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_{3-\delta}$ (LSGM)

**Anode Materials**

- NiO/YSZ (50% YSZ by weight)
- NiO/GDC (50% GDC by weight)

**Cathode Material**

- $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.98}\text{MnO}_{3-\delta}$ (LSM)
- La$_{0.6}$Sr$_{0.4}$Fe$_{0.8}$Co$_{0.2}$O$_{3-\delta}$ (LSCF)
- La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ (LSC)
- La$_{0.8}$Sr$_{0.2}$FeO$_{3-\delta}$ (LSF)
- Sm$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ (SSC)
- LSCF/GDC (50-50% by weight)
- LSC/GDC (50-50% by weight)
- LSF/GDC (50-50% by weight)
- SSC/GDC (50-50% by weight)
SOFC Components

Electrochemical performance and durability of 10 × 10 cells

Cell voltage, mV

Power density, W/cm²

Time, hour

Active cell area: 16 cm²
Anode gas: 24 l/h H₂ with 4 % H₂O
Cathode gas: 140 l/h air
Temperature: 750 °C

0.25 A/cm²

Z” (Ω cm²)
Z’ (Ω cm²)

Single cell
Sealing
Interconnect
SOFC Integrated Modules

- Cutting-edge research
  - Sealing material and technology
  - Novel stack structure design
  - Mult-field modeling and test
  - Degradation factors and mechanism of stack
- Industry technology
  - Integrating technology—Know How
  - Repeatability and reliability
  - Standardization and modularization
  - Characterization and test method
  - Product standard

- Integrating process of stack
  - Establish standard packaging technology
  - Realize mass production of stacks
SOFC Power Generation System

Flow chart of kW-level SOFC system

SOFC power

generation system

HS-201-1000 SOFC power generation system:
- Size: 1430 L × 1060 W × 1850 H (mm);
- Weight: 300Kg;
- Output: 1kW;
- Maximum electrical efficiency: 50%;
- Thermal efficiency: 25%;
- Overall efficiency: 75%;
- Rated output voltage: AC 220V ±5%;
- Frequency: 50HZ;
- Noise standards: ≤ 50 dB;
- Operating ambient temperature: -40°C-50°C
SOFC Demonstrations

Fuel Cell Committee

Project achievement

Standards and Test Center

苏州华清京昆新能源科技有限公司

Disney

晋煤集团

新奥集团

Demonstrations

工业技术推广

市场运营

Expended Application

渭南项目

南京科利尔公司

Mobile power generation, automotive industry

Waste biomass generation

Industrial Technology Promotion

广东清大公司

Demonstrations
The Beginning of SOFC Industry in China

◆ Suzhou Huatsing Jingkun Power System Co., Ltd: Established in 2010, specialized in SOFC industrialization, have achieved substantially all of the SOFC technologies;
  - January 2013, obtained 11 million venture capital;
  - December 2014, demonstration and application of carbon-based fuel SOFC system (700 million);
  - December 2015, obtained 200 million venture capital from Tsinghua for the manufacture and demonstration of SOFC power generation system.

◆ ChaoZhou Three-circle (Group) Co., Ltd.: income of over 200 million on SOFC electrolyte plate;

◆ G-cell Technology Co., Ltd.: established by China University Technology and Japan SHINCRON Co., Ltd. in April 2013, aiming to promote the industrialization of SOFC CHP system as well as related materials and applications.

◆ Ningbo SOFCMAN Energy Technology Co., Ltd.: established by Legend Star in August 2014, aiming at the industrialization of SOFC.
36 patents:

◆ Single cell
Patent No.: ZL 02 1 29594.8

◆ Sealing material
Patent No.: ZL 02 1 47179.7

◆ Interconnector
Patent No.: ZL02155409.9

◆ Power generation system Patent
No.: ZL2014.20393678.6

◆ Key materials preparation and mass production of components
◆ Cell stack assembly and power generation system integration
◆ Demonstration projects

Materials ➔ Cells ➔ Integration module ➔ System ➔ Users
Suzhou Huatsing Jingkun Power System Co., Ltd

Founded in 2010
Cooperated with universities
Undertaking national "973" project, and so on
Put forward the SOFC industrialization in China

- Materials
- Cells
- Integration module
- System
- Users
Low degradation:
After 1 year operation at 750°C, electrical efficiency still over 60%.
(Previous achievement by CFCL)

Thermal cycle test:
After 24 repeated thermal circle, average of 0.15% voltage degradation per cycle and without leakage. (Previous achievement by CFCL)

Product name: C1 stack
1. 1 kW power;
2. Stack efficiency degradation < 0.2%/khrs @ BlueGen system.
3. Stack DC electrical efficiency > 65% @ BlueGen system.
4. Thermal cycle resistance.
Product name: C1 stack
1. 24V;
2. 1kW
宁波市福人能源技术有限公司
Ningbo SOFCMAN Energy Technology Co., Ltd.

A stack module

1. Electrical power output of 1300W
2. Fuel utilization of 94.3%
3. Electrical efficiency of 72.5% (LHV).

Founded in 2014
Opportunities and Challenges of SOFC in China

- Suzhou Huatsing Jingkun Power System Co., Ltd
- ChaoZhou Three-circle (Group) Co., Ltd.
- G-cell Technology Co., Ltd.
- Ningbo SOFCMAN Energy Technology Co., Ltd.
- The others ……

There still is a long way to go ……

路漫漫其修远兮……

——《离骚》- 97/370 屈原
THANK YOU