Carbon-Based SOFC Power System in China

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Technical Committee for Standardization of High Temp. Fuel Cell Director

Contents

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

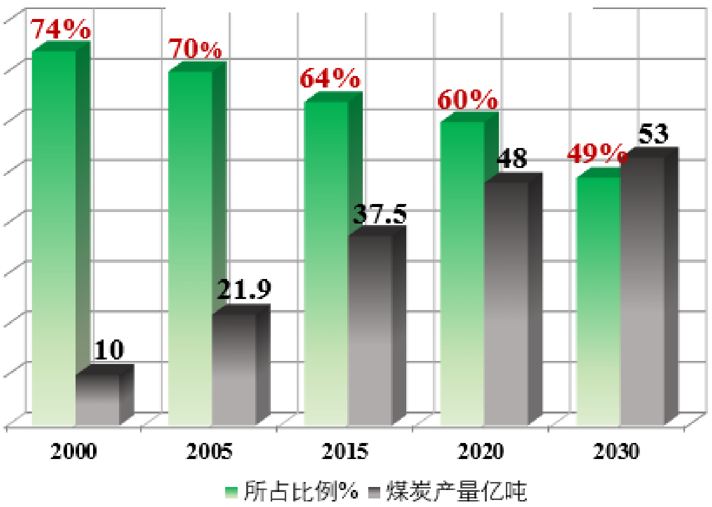
◆ **National demand:** **Efficiency and Environmental Protection**

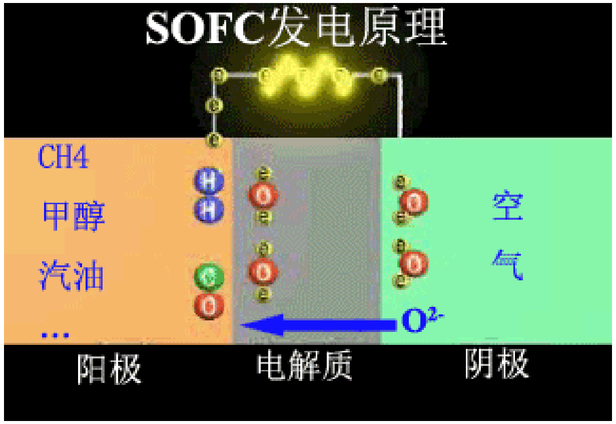
国家重大需求：提高煤炭利用效率，降低煤炭用量，减少环境污染

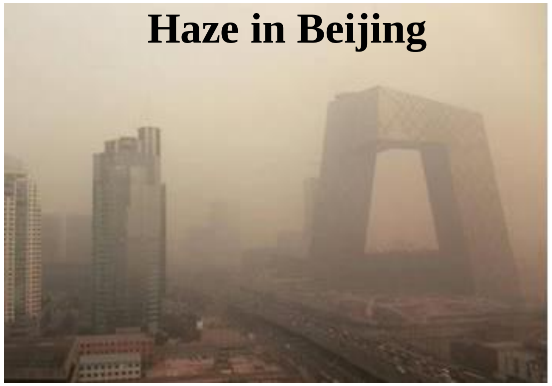
◆ **Solution: New power generation technology----Carbon-based SOFC power generation system**

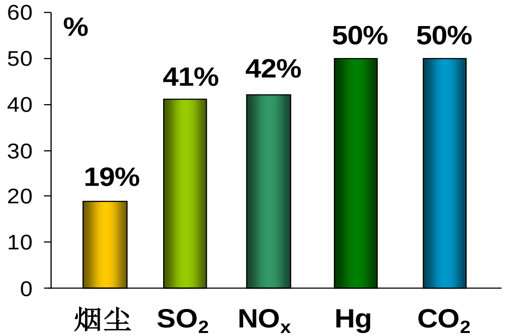
解决方案：寻求新的发电技术—碳基燃料固体氧化物燃料电池(SOFC)发电系统

煤炭是我国基础能源









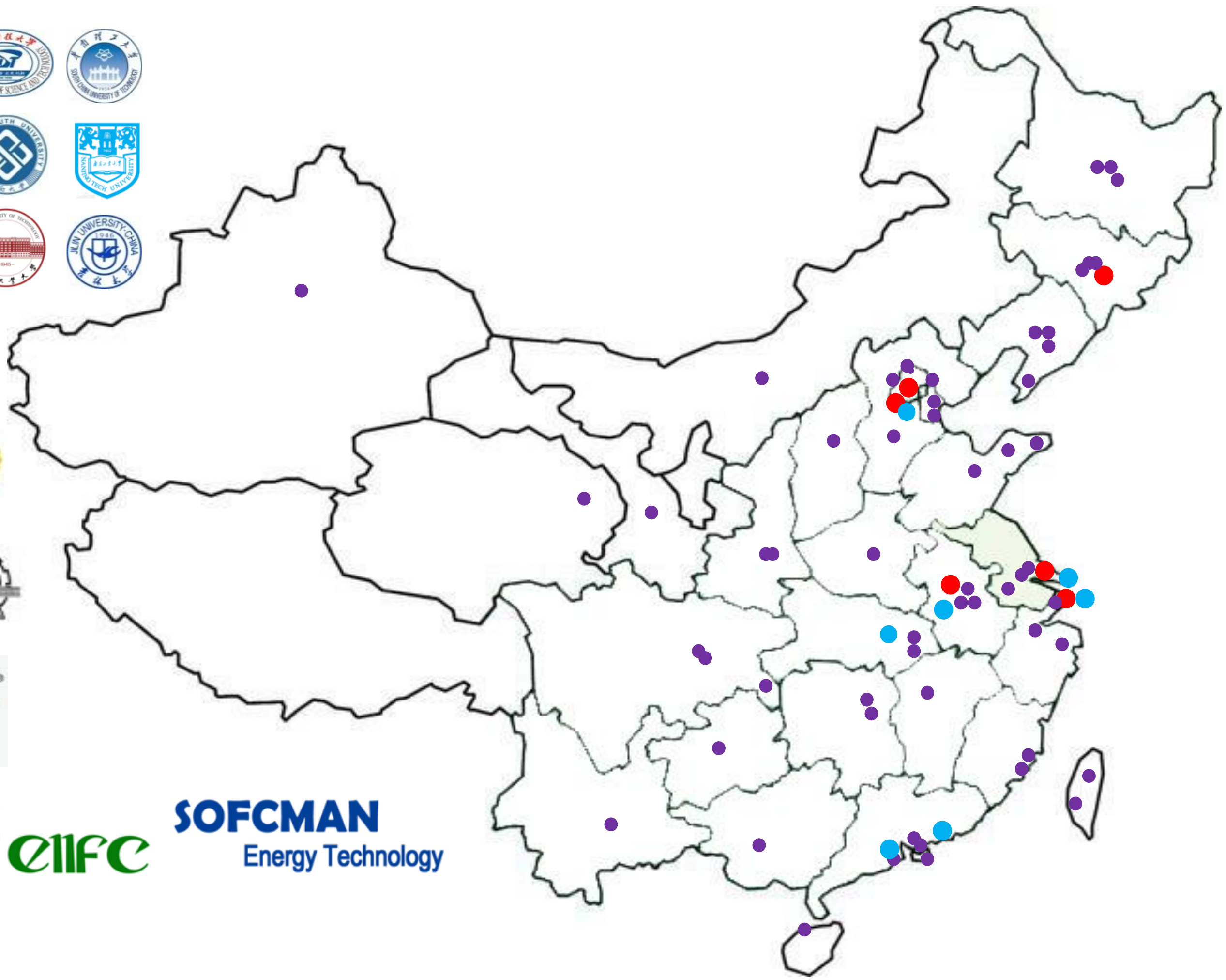
Major Pollutions based on Coal Power Plant

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

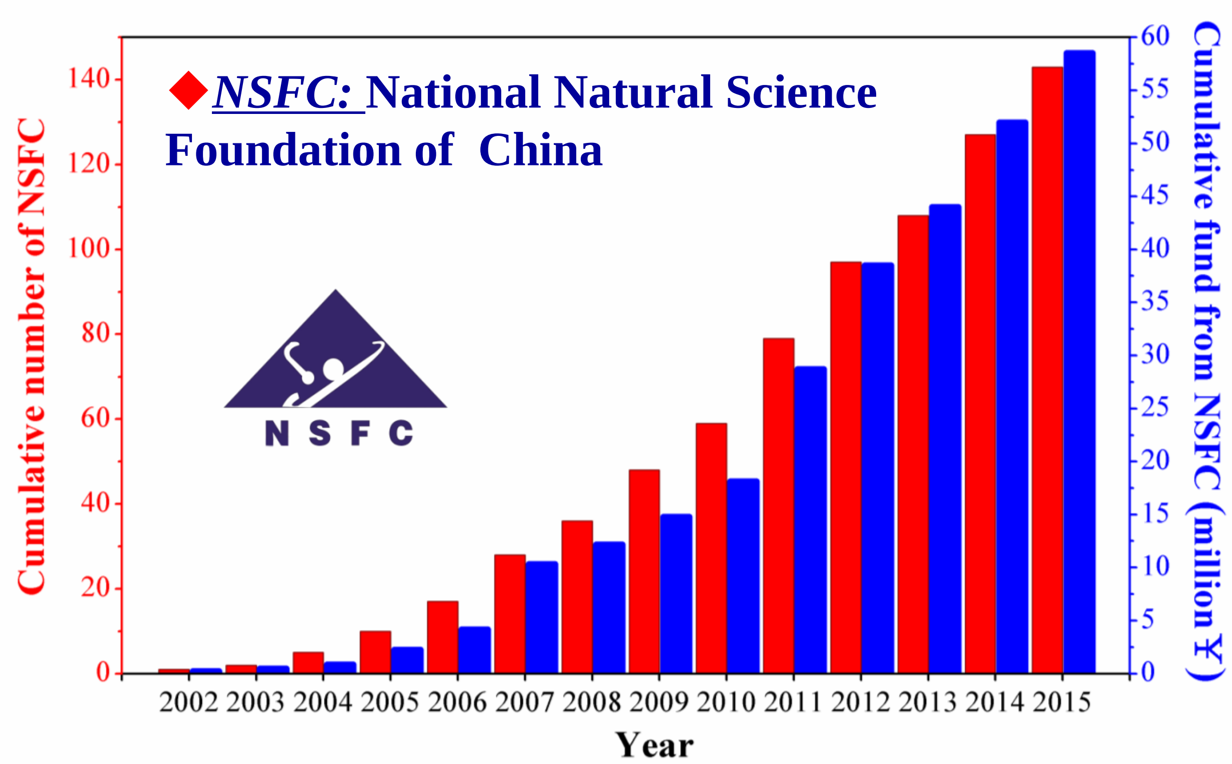
- During 2002-2015, more than 140 projects were supported by the NSFC, with about ¥60 million in grants.
- In the National Medium-Long-Term Program for Science and Technology Development (2006-2020), the SOFC is set as one of the most important technologies for distributive energy supply.

◆New materials

◆New designs

◆New theories

◆New methods



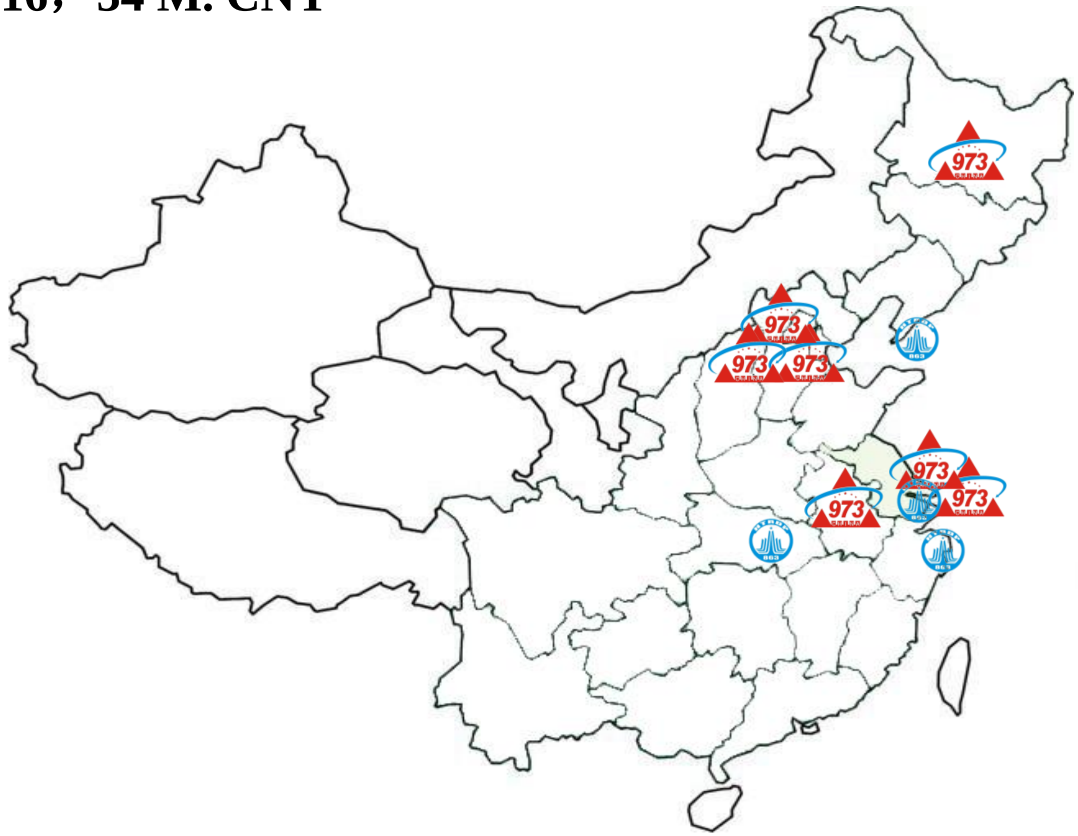
Cumulative number and fund of NSFC program related to SOFC from 2002 to 2015

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**



12th "Five-Year Plan"—— 863 Program

Key Technologies of Fuel Cells and Distributed Power Generation System

2011-2014，80 M. CNY

	TASK	RESPONSIBLE
1	Fuel Cell technology Integrated Natural Gas Reforming to H_2	DICP
2	1 kW AAEMFC (Alkaline Anion Exchange Membrane FC)	DICP
3	Distributed PEMFC Power System	DICP
4	25kW Tubular SOFC Stack	DICP
5	25kW Planar SOFC Stack	NIMTE
6	Integration of 5kW Intermediate Planar SOFC Independent Power Generation System	HUST,SIC

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 CO_2 Near Zero Emission

CO_2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

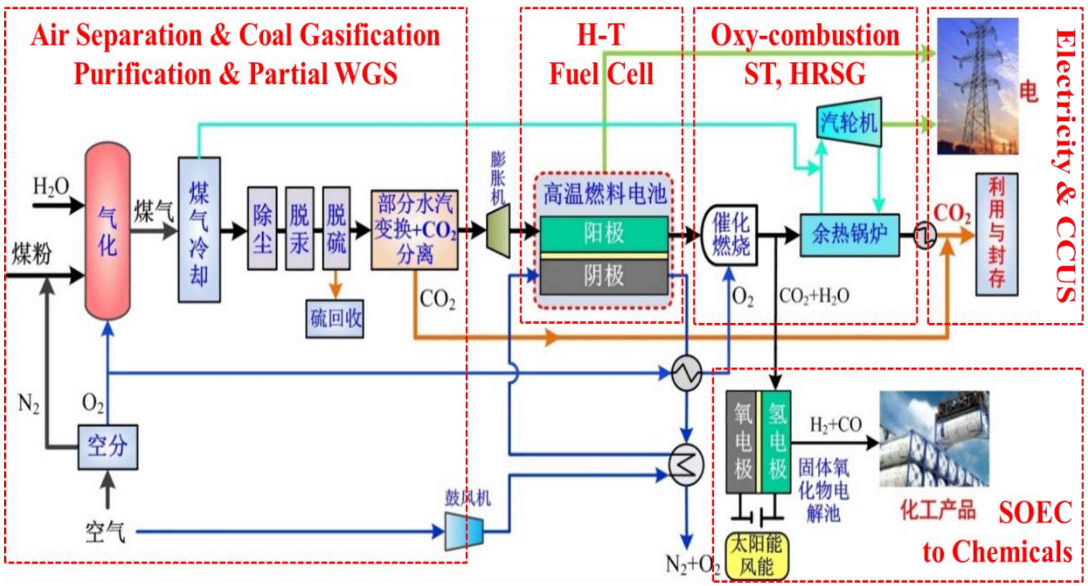
Shenhua Group

Chief Scientist: Prof. Suping Peng

Coal Gasification Power System Combined CO_2 Near-zero Emission

Objectives

- Mechanism, system design, and key equipment manufacturing technology of Integrated Gasification Fuel Cell (IGFC) power generation
- The MW-scale CO_2 near-zero emission IGFC demonstration system
- Schematic design and technological packages for 100 MW-scale CO_2 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 CO_2 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 CO_2 capture ≥91%

3）Schematic design and technological packages for 100 MW-scale IGFC system, with CO_2 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)》

9. Hydrogen and Fuel Cell Technology Innovation, **(NDRC and NEA, 2016.4.18)**

- **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**

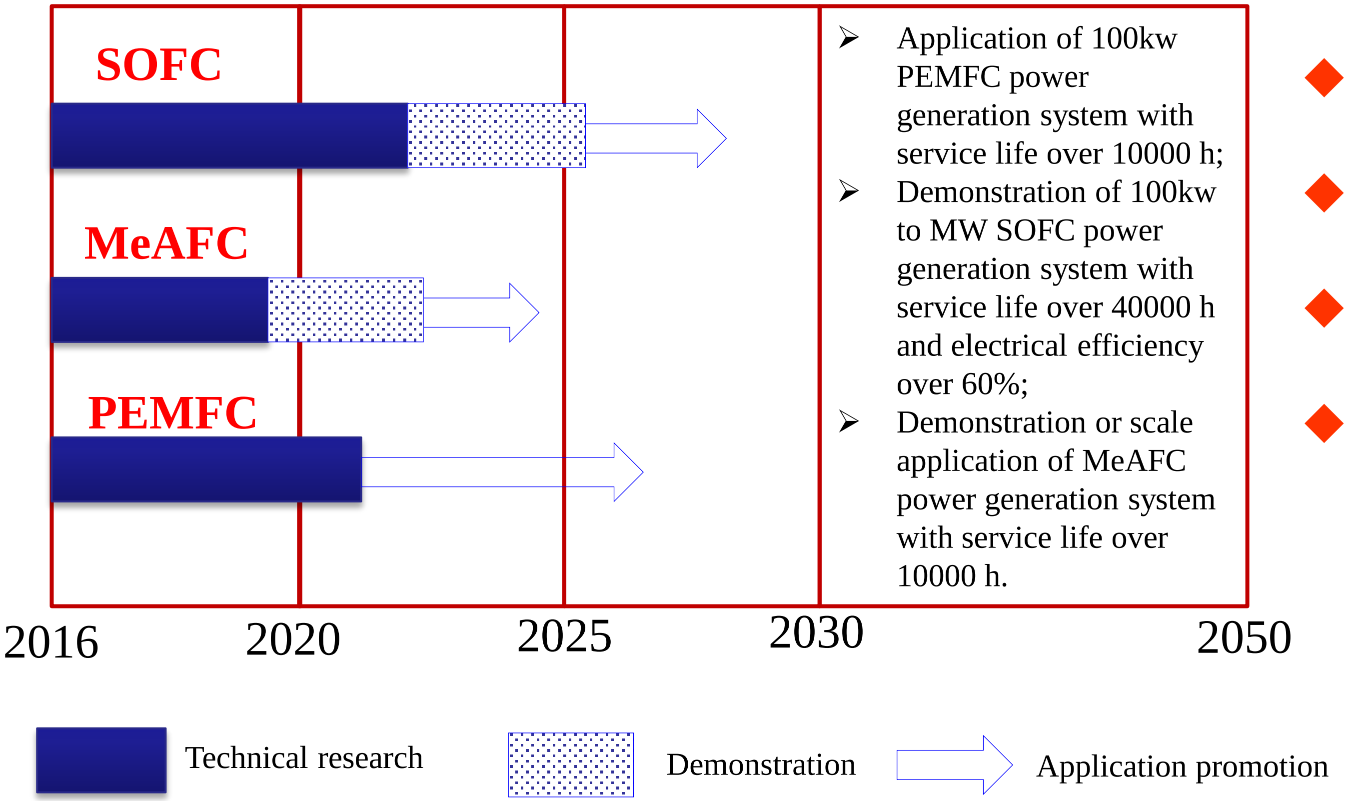
Demonstration of Hundreds KW to MW level SOFC-based distributed power generation system with efficiency over 60; Developing distributed power station for remote cities and industrial enterprises.

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**

How to do for SOFC in China?

- ◆2016.11, Chinese Fuel Cell Committee　成立了中国能源研究会燃料电池专业委员会
- ◆2017.03, Technical Committee for Standardization of H-T Fuel Cell
  成立了能源行业高温燃料电池标准化技术委员会(国能综科技[2017]115号）
- ◆ 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?


中国能源研究会

中国能源研究会关于成立燃料电池专业委员会的决定


关于同意作为中国能源研究会燃料电池专业委员会支撑单位的函

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

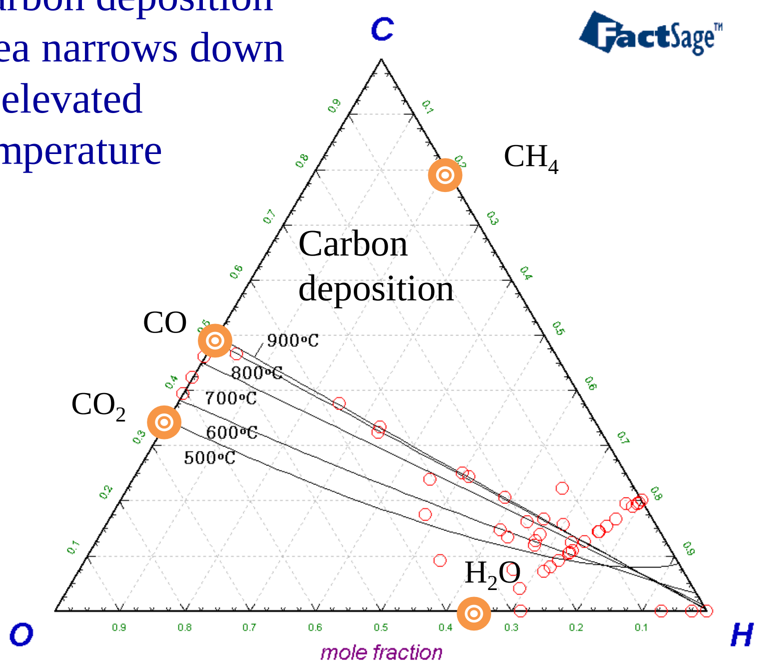
3. Conduction mechanism and theoretical system

- 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

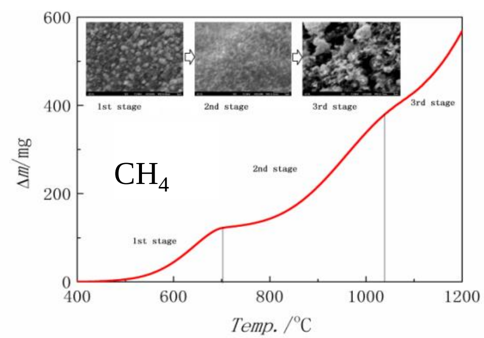
Carbon deposition area narrows down at elevated temperature

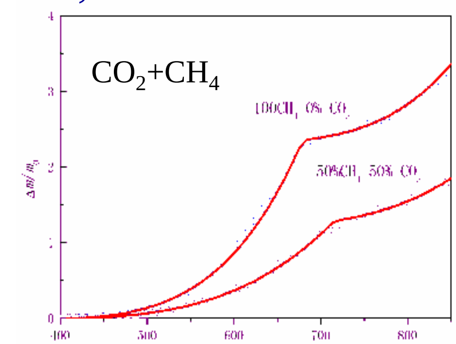


Carbon deposition area of C-H-O system

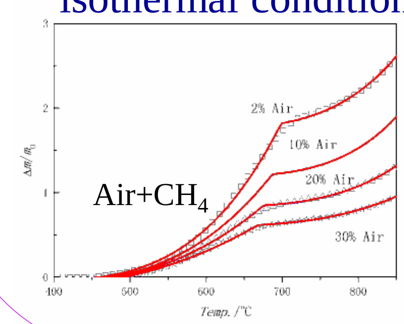
➢Dynamic mechanism of carbon deposition resistance

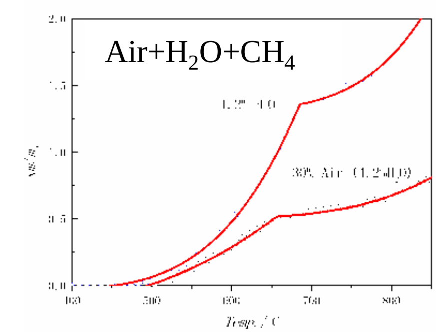
✓ Carbon deposition rate can be reduced by adjusting the parameters of *P*, *T*.





✓ Coking kinetics of CH_4 on Ni under non-isothermal conditions





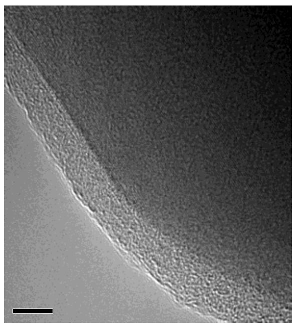
➢Carbon deposition can be reduced or even removed through adjusting gas composition.

Ni-YSZ Cermet Anode Modification

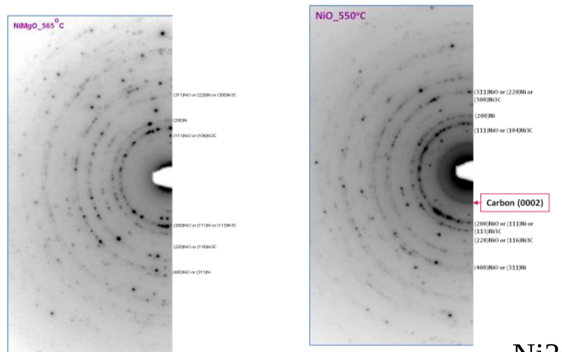
Influence factors of coke resistance on catalyst surface: structure and acidity

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

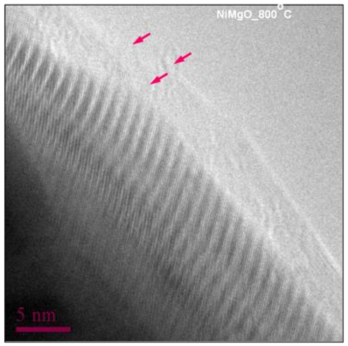
The high activity and stability can be maintained by loading MO (M=Mg, Ba, Sn) on Ni-YSZ anode with CH_4



2.5wt% MgO coated NiO

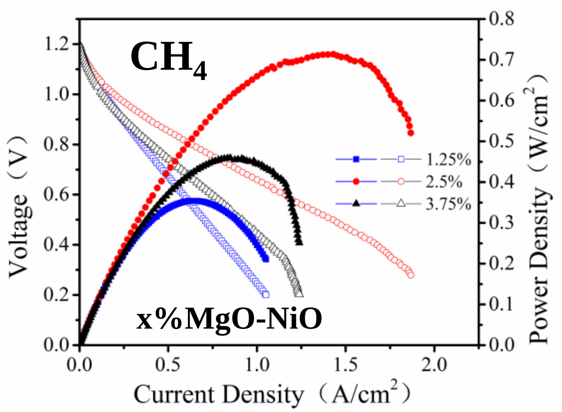


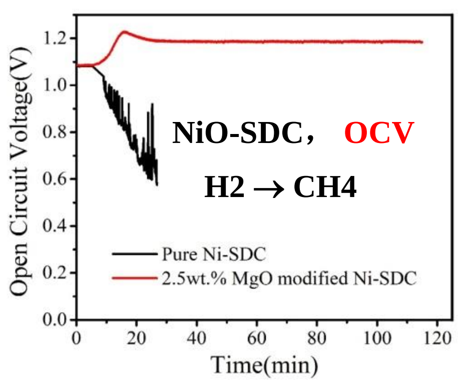
MgO modified Ni show good coke resistance

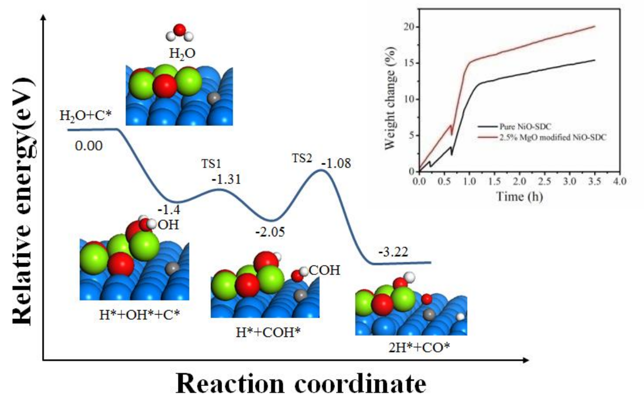


Dislocations (see arrows) are introduced to relax the strain resulted from the decomposition of Ni3C in NiMgO.

Ni3C is an intermediate phase during carbon deposition process







➢H_2O easily dissociated on MgO, forming COH with the deposited carbon.

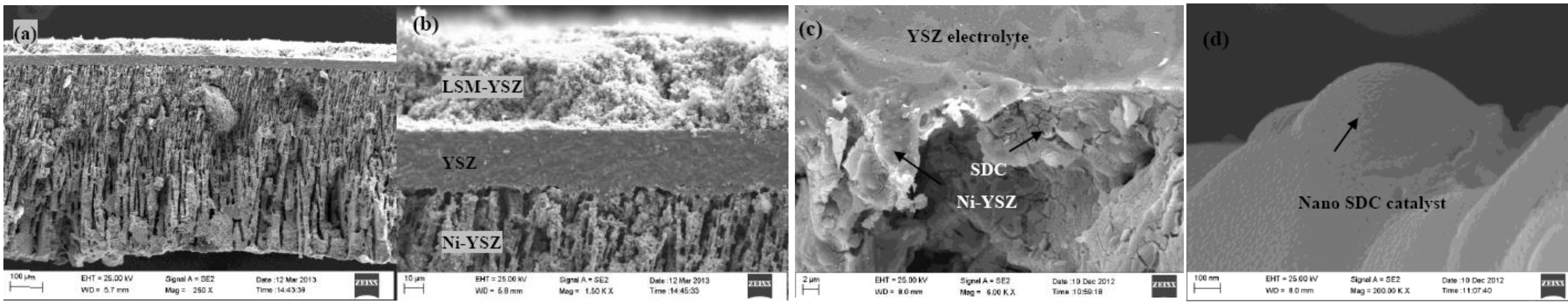
➢COH dissociated on Ni surface, forming CO, and then oxidized into CO2 by O radical.

Anti-carbon deposition by load of nano-SDC

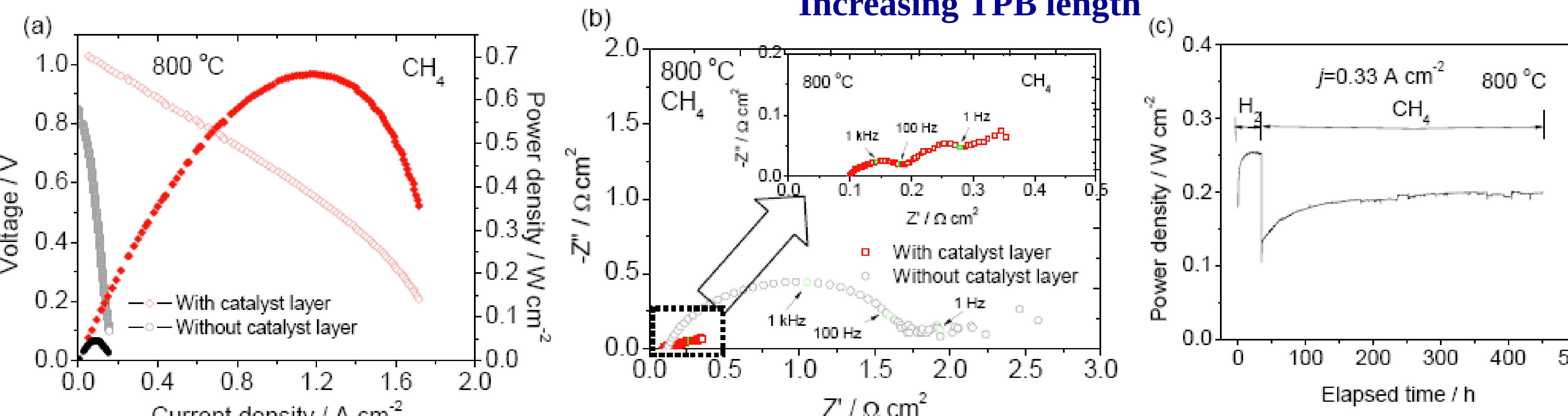
电极上负载纳米SDC改性具有普适性

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



Increasing TPB length



Improving catalytic activity **Reducing polarization resistance** **Stable operation in CH_4**

Yu Chen, Han Minfang, et al , Nano Energy(2014) 10：1–9

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

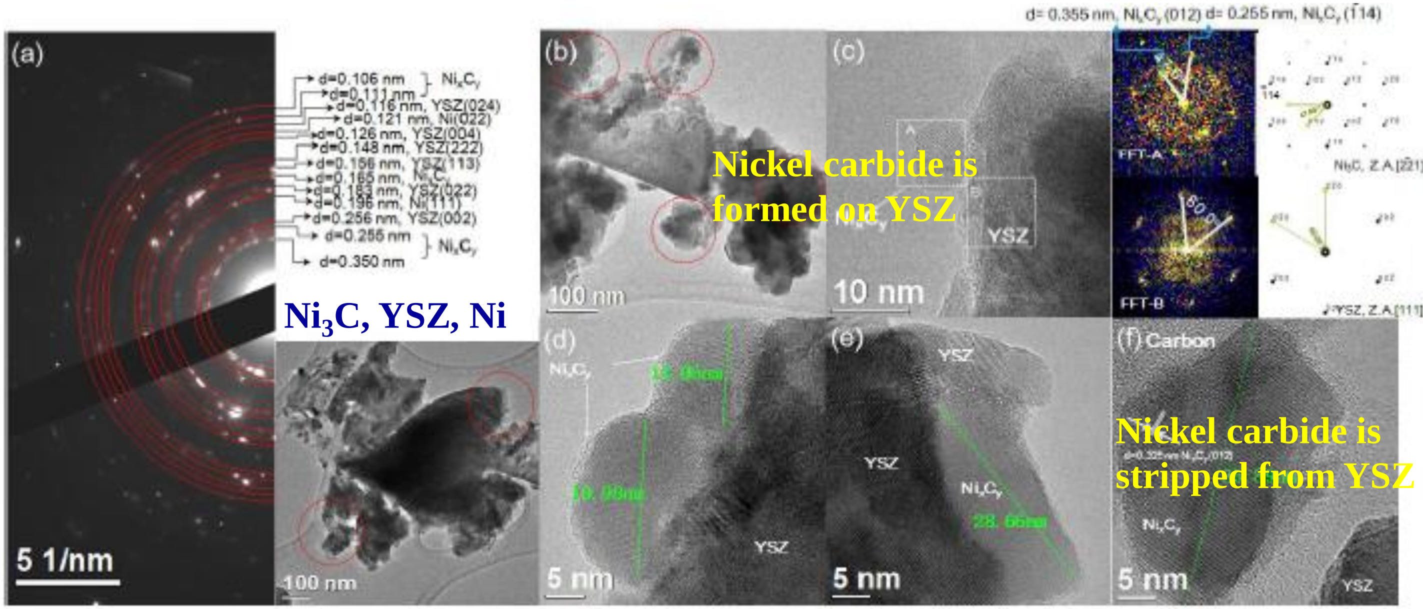
阳极中负载SDC有效抑制碳化镍形成提高了碳基燃料中的稳定性

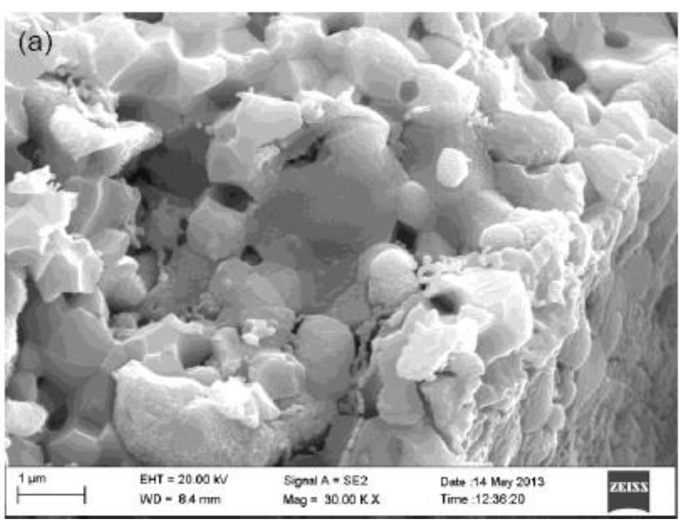
Nickel carbide formed without loading SDC.

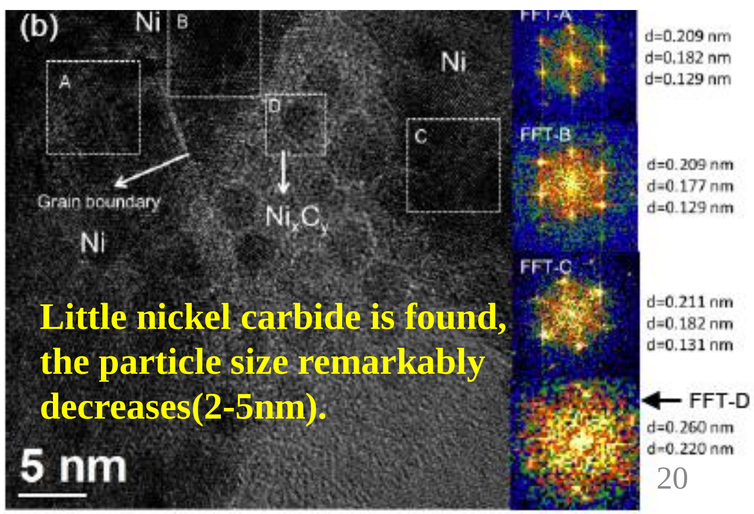
Anti-carbon deposition mechanism:

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

纳米SDC层有效抑制碳化镍形成-积碳原因，提高镍基阳极抗积碳性能



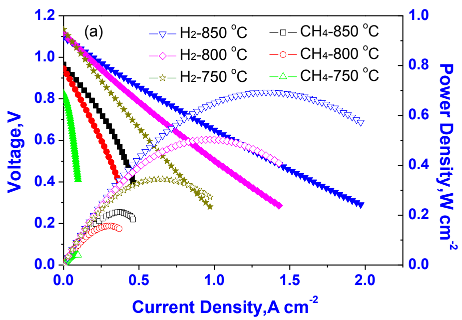


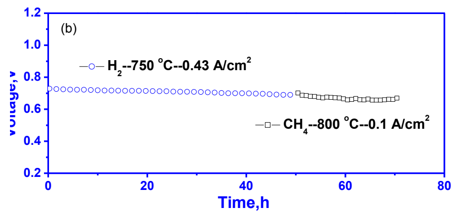


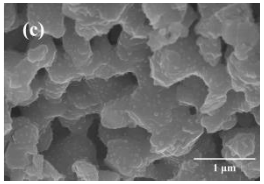
Novel Perovskite Anode Materials

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

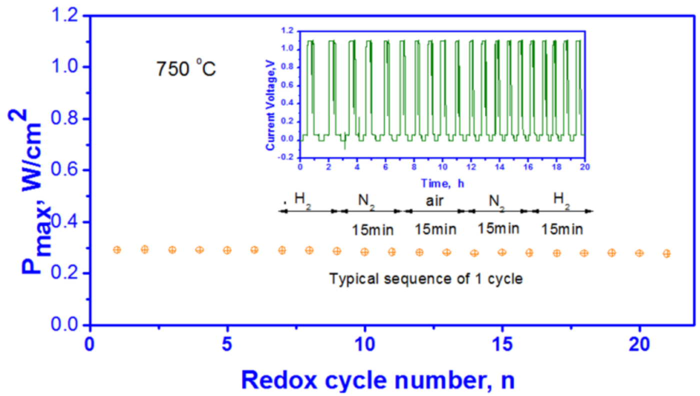
◆$La_{0.4}Sr_{0.6}Co_{0.2}Fe_{0.7}Nb_{0.1}O_{3-\delta}$(LSCFN)







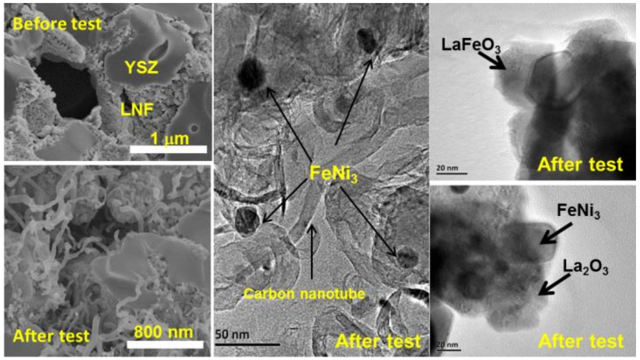
➤Directly hydrocarbon fueled



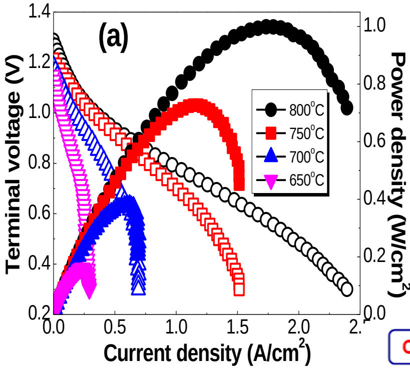
➤Excellent stability under hydrocarbon fuel

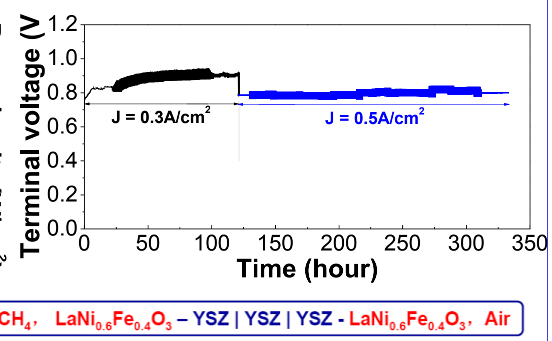
➤Excellent redox cycling stability

◆$LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ (LNF)



➤In-situ precipitated Nano Co-Fe particle.





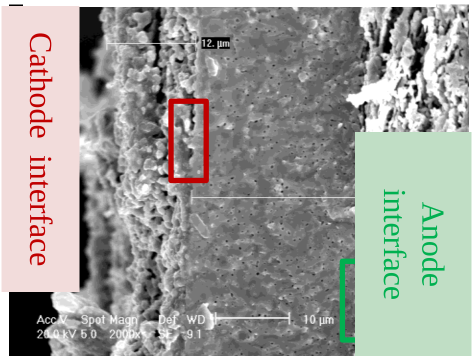
➤Nano alloy particles enhanced the electronic conductivity and fuel catalytic activity.

J. Electrochem. Soc.-2015-F718-21

Tri-layer Structure Design

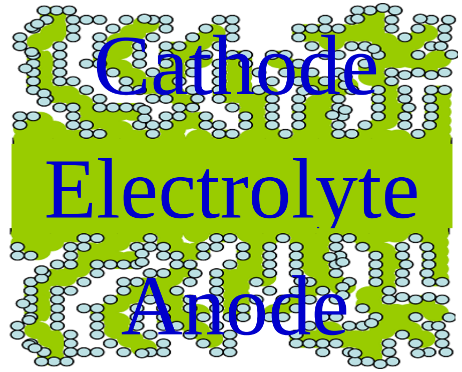
——Higher stable performance with continuous interface

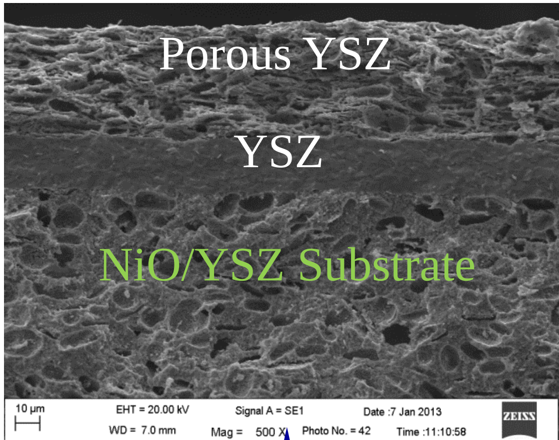
Normal issues in sandwich-structure



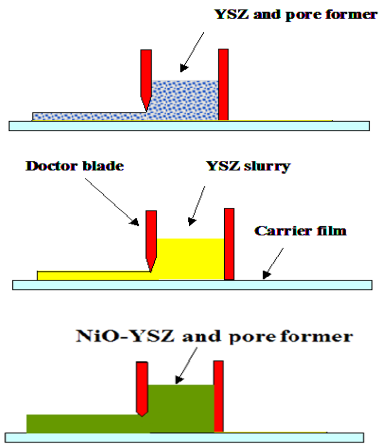
Crack, peeling off and incompatibility etc..

Design and fabrication of tri-layer cell





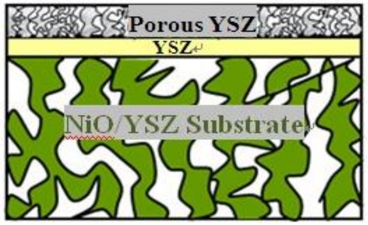
Porous cathode support||densified electrolyte||porous anode support

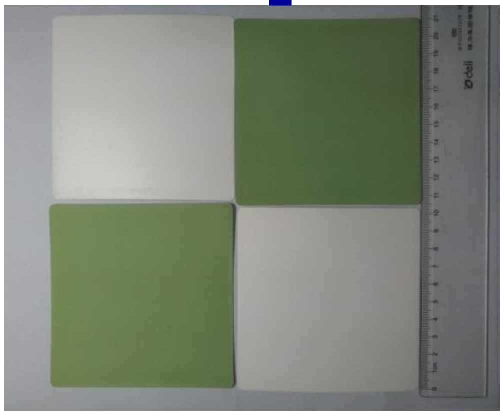


Tri-layer (High stable matrix)

Co-press

Co-sinter



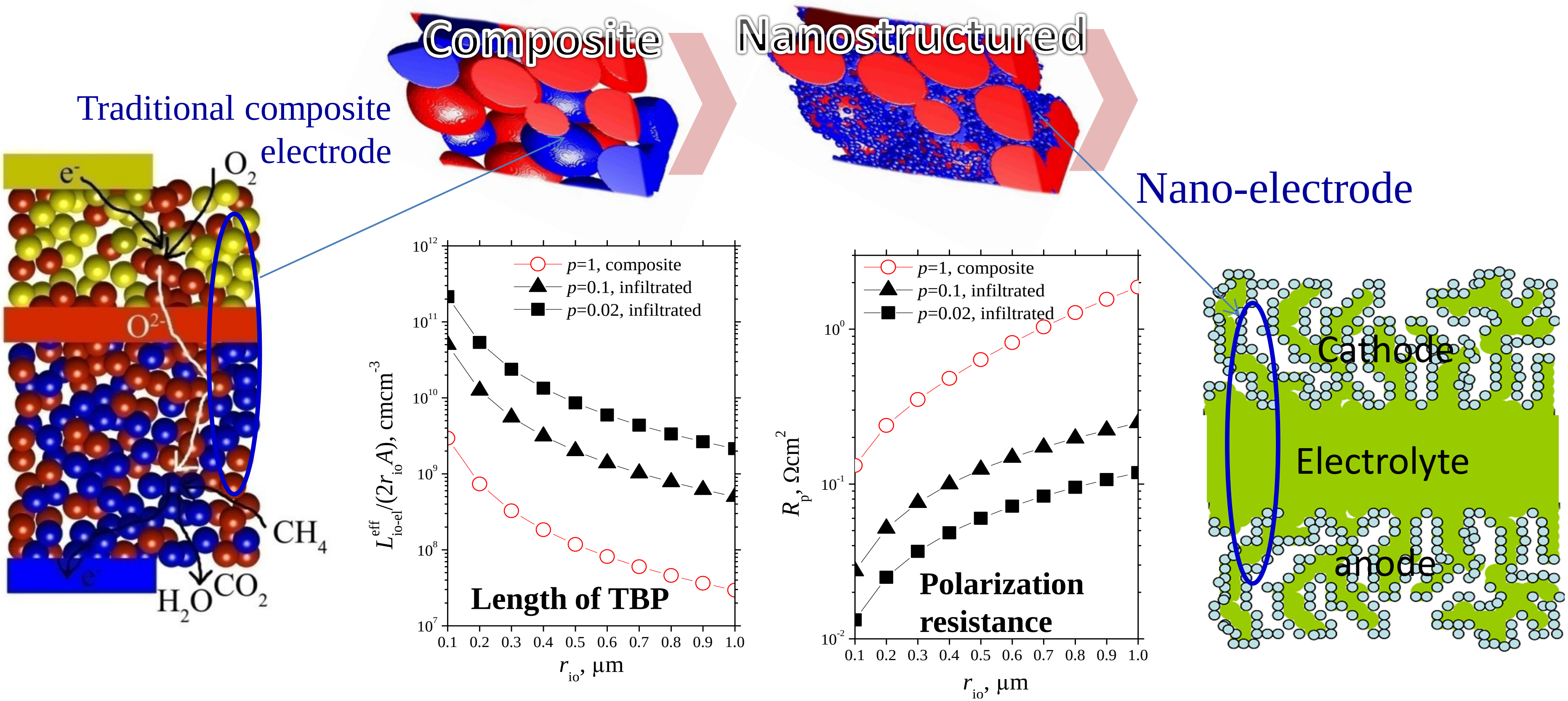


- **Tri-layer structure:** Eliminate the interfacial problems, improving the long-term stability of SOFC.

Tri-layer Structure Theoretical Foundation

—Higher performance with nano-eletrode

TBP is the main place of electrode reaction, structural design of electrode is essential



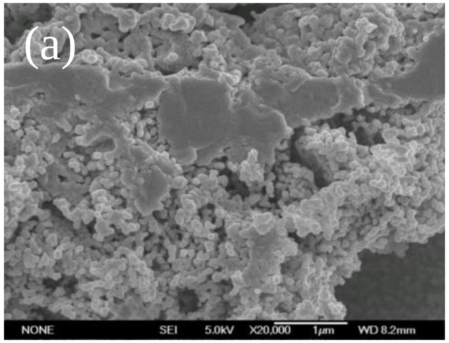
- In situ loading of nano-electrode can significantly improve the TBP length and reduce electrode polarization resistance, laying the theoretical foundation for the high-performance.

(*J Power Sources* 218 (2012) 254-260；J. Electrochem. Soc., 162 (1) F33-F39 (2015)

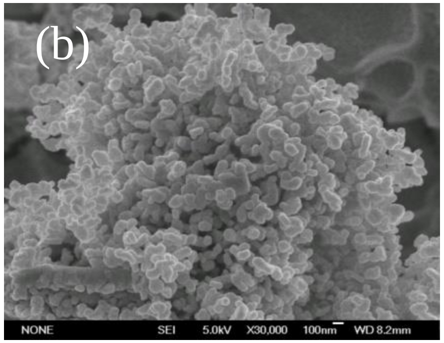
Optimization of In-situ Loading Nano-cathode Materials

优化了液相负载纳米阴极材料组成

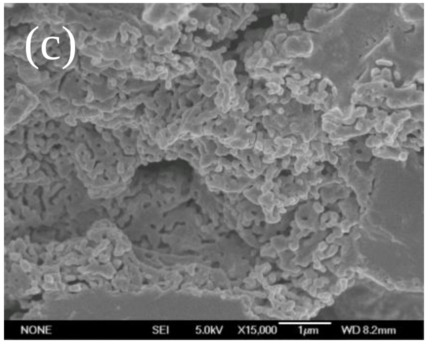
- In situ loading of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$（LSCF）



Infiltrated LSCF layer with thickness of ~2μm

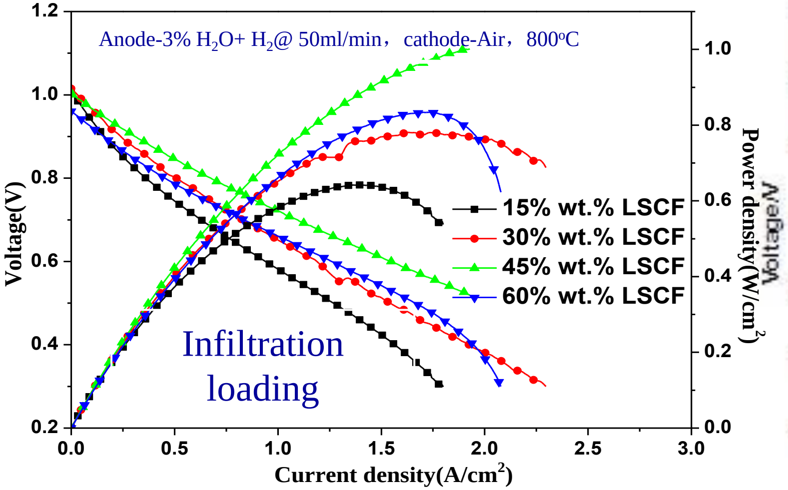


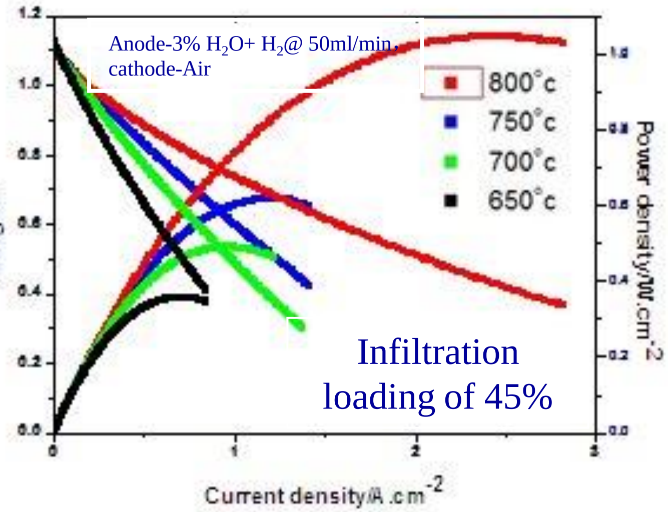
Nano particle of LSCF



No extra phase formed between LSCF and YSZ interface

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





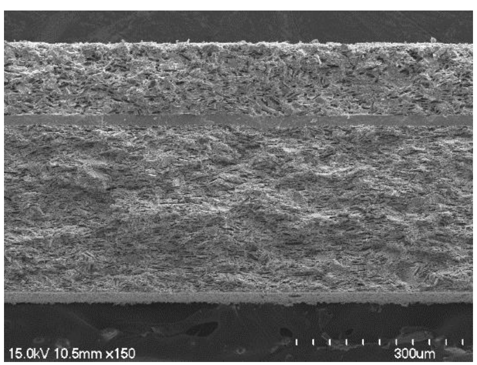
Achievements:

- Uniform loading ;
- Optimal loading amount of 45wt.%.

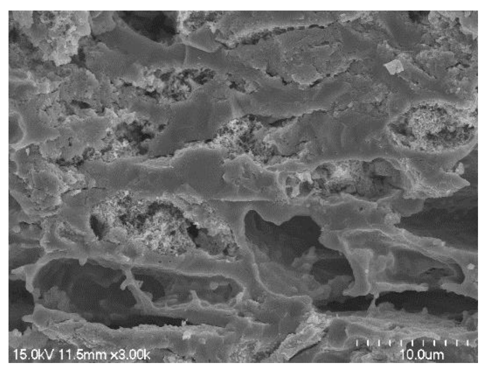
Tang Dan, Minfang Han, J. Fuel Cell Sci. Technol 12(1), 011001 (2015)

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

Anode supported tri-layer single cells



Cross sectional microstructure



Nano-structure of LSCF cathode

NiO-YSZ || YSZ || YSZ-LSCF

Achievements:

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

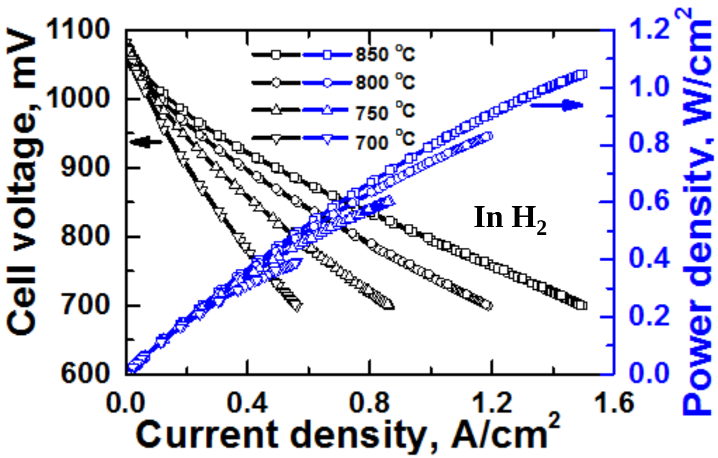
  应用原位液相负载纳米电极技术，获 得10cm × 10cm（工业产品尺寸）一体化单电池

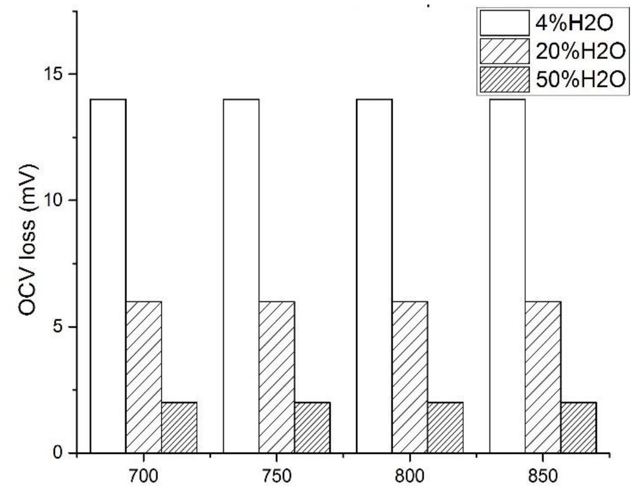
- **Pilot production with stable preparation process**

  完成了中试，稳定了制备工艺，实现批量化制备

Third-party Evaluation of 10cm×10cm Tri-layer SOFCs

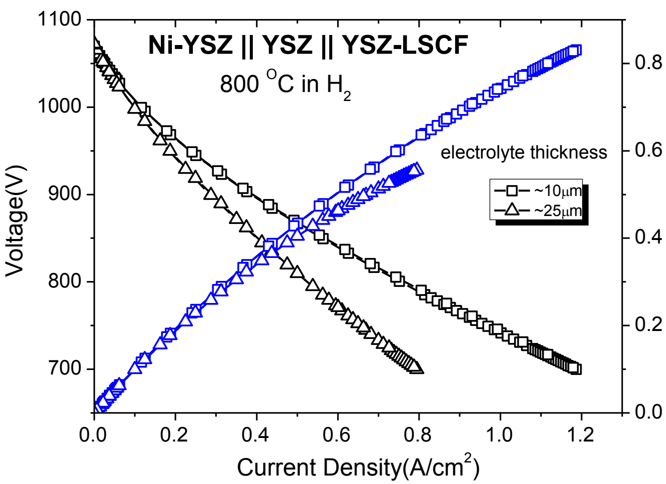
10cm × 10cm一体化电池第三方评价

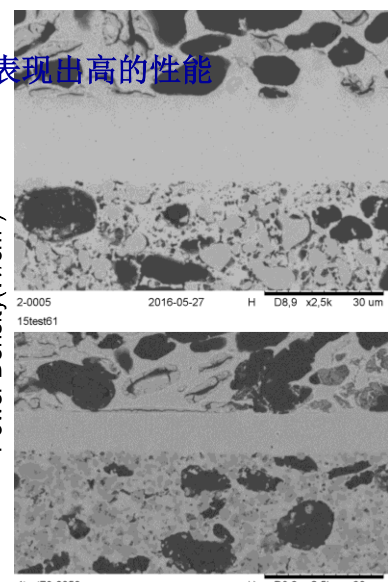


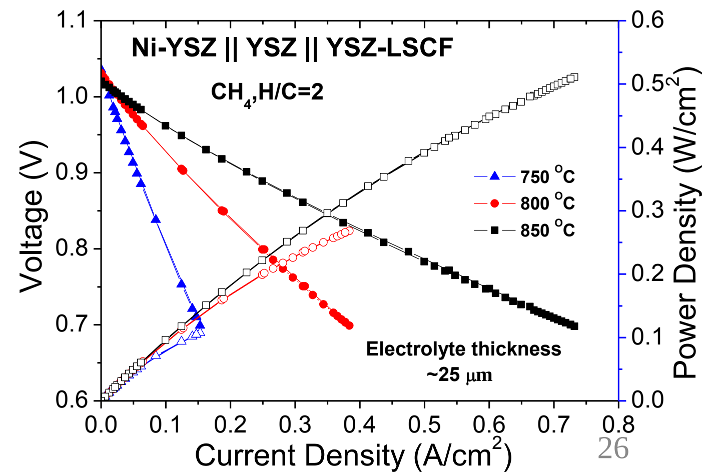


➢ **High performance under hydrogen and (simulated) methane reforming gas was validated by DTU.**

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

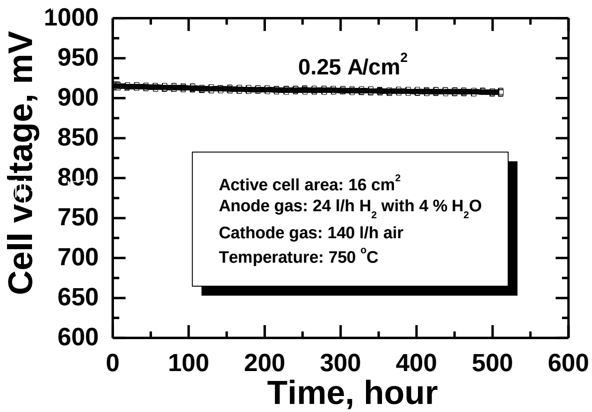


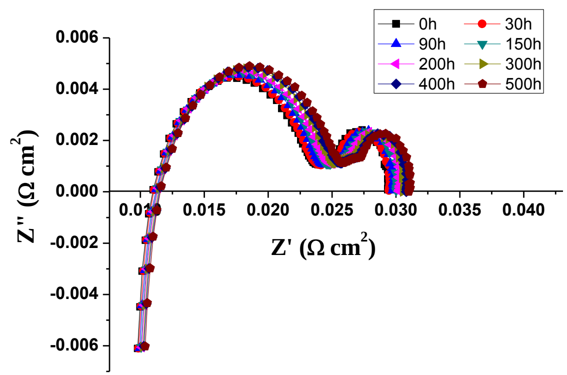


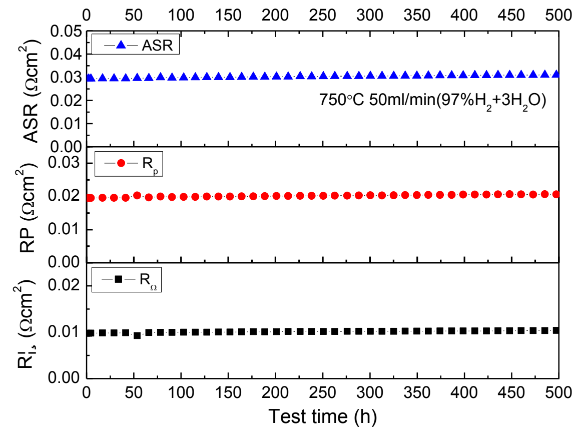


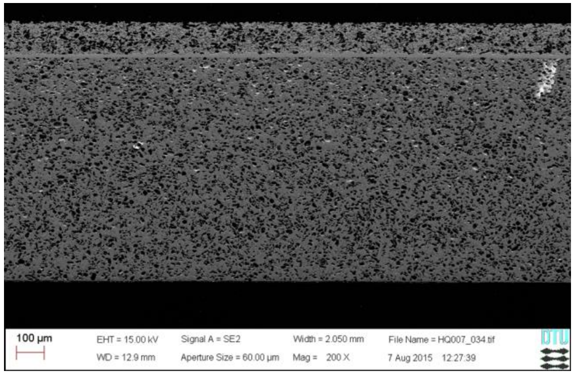
High Performance and Stability for 10×10cm Cells（8/8）

10cm × 10cm tri-layer SOFCs show high output performance and good stability

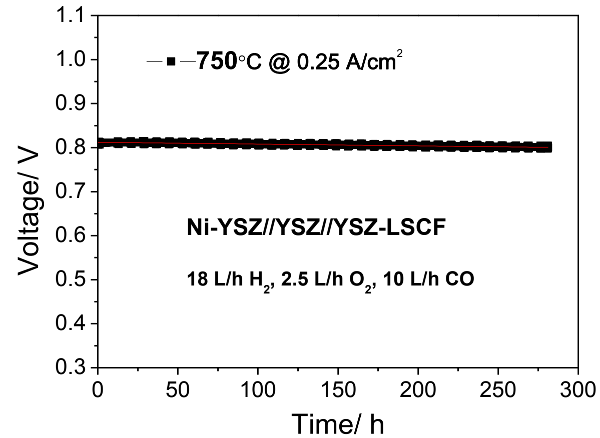








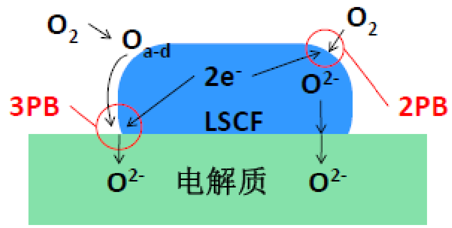
- Third-party evaluation: Technical University of Denmark, Risϕ Laboratory;
- Stable operation at 750°C.



Electrons and Ion Transport Mechanisms in Multiphase System

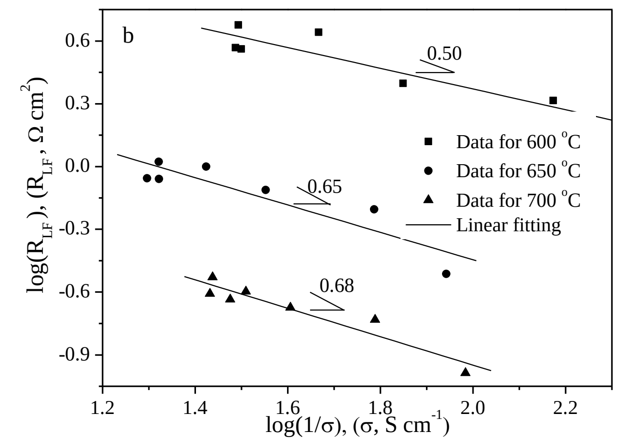
1 Oxygen reduction process at Cathode TBP

- ✓ 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

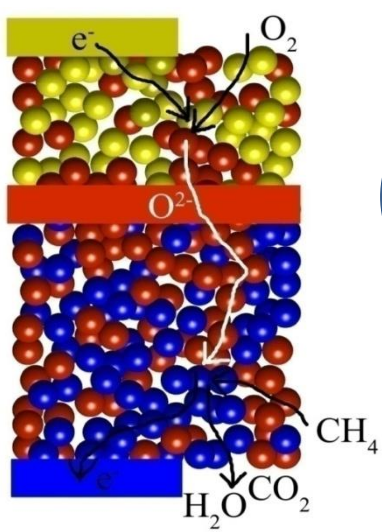
- ✓ Cerium oxide intermediate layer $R_p \propto \sigma^l P_{O_2}^n$

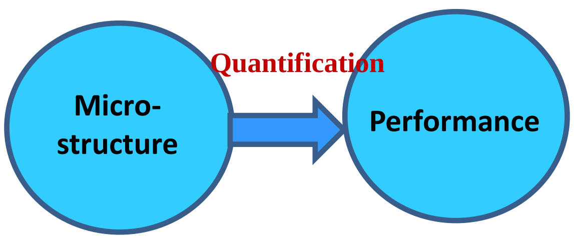


The linear relationship of polarization resistance Rp of LSCF to $ln\sigma$

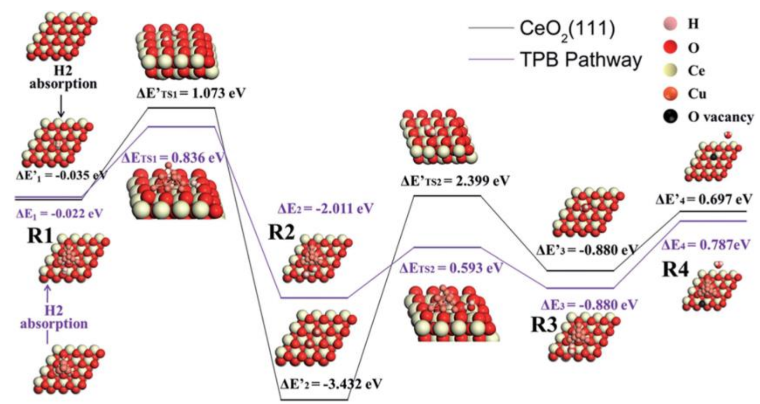
3 Anodizing process at TBP

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





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



Formation and Evolution of Multiphase Interface

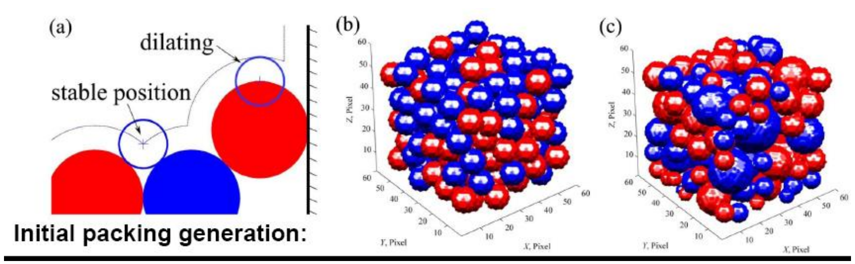
1 Formation and evolution of 2PB、3PB in composite electrode

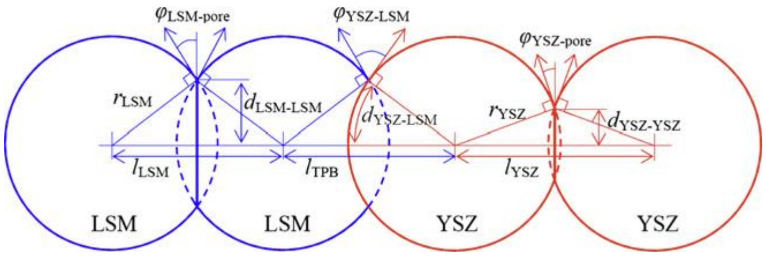
- ✓ Propose the kMC and analytical sintering model for composite electrode
- ✓ Predict the formation of 3PB and 2PB

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



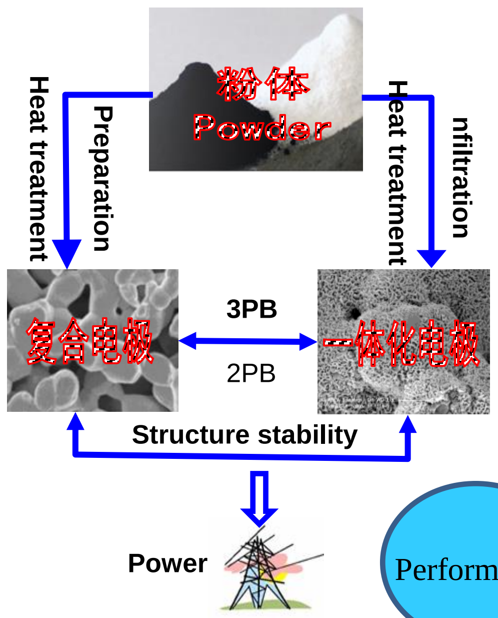


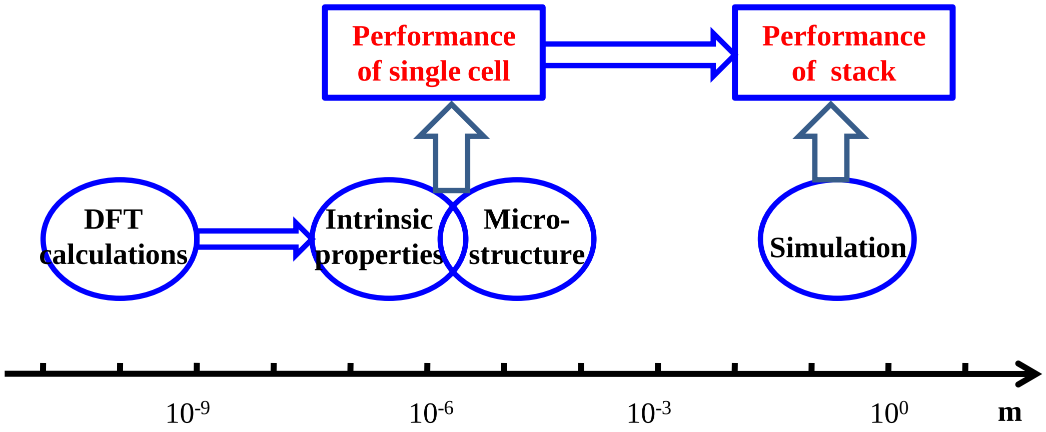
kinetic model of Monte Carlo (kMC)

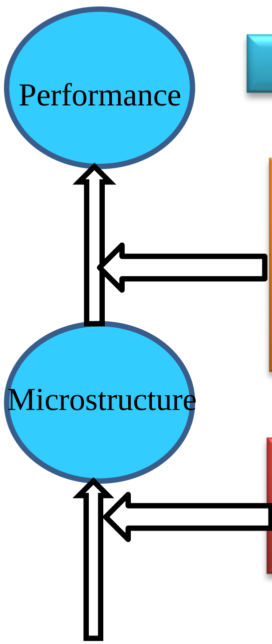
Analytic Sintering Model

Xia C.R., Zhang YX, *Int. J. Hydrogen Energy* 37 (2012) 3392-3402
Xia C.R., Zhang YX, *J. Am. Ceram. Soc.* 97 2580-2589 (2014）

SOFC Theoretical System
——From Powder To Power







Scientific issues

Construction of high-performance electrode and its electrochemical behavior

Electron and ion transport mechanism in multiphase system

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.

Evolution of multiphase interface

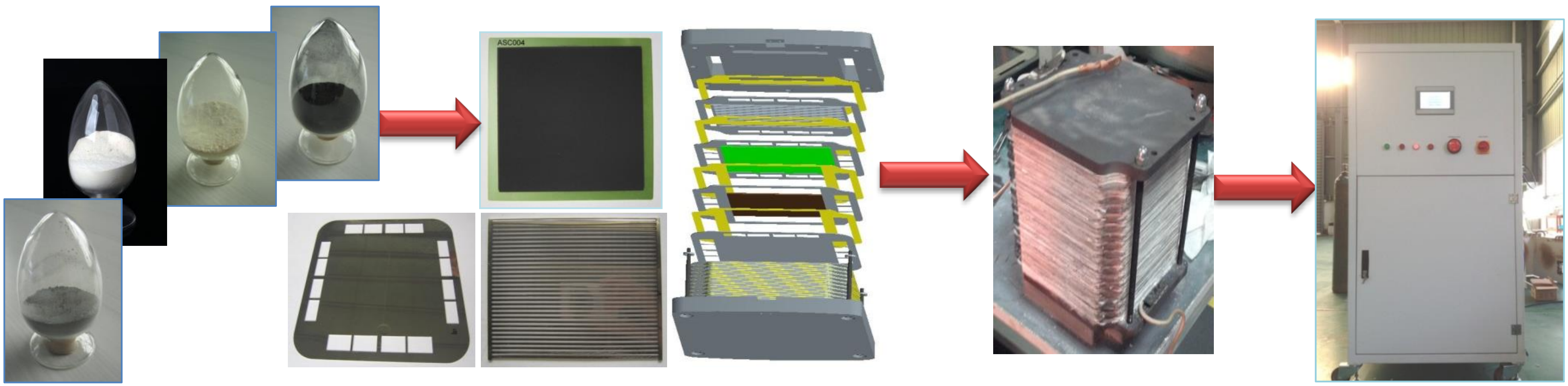
1. Formation and evolution of 2PB and 3PB;
2. 2PB and 3PB in tri-layer SOFC electrode;
3. Stability under electric field;
4. Mechanical model of thermal cycling.

Contents

- SOFC Target in China
- SOFC Technical Development
- SOFC Industrialization

Progress in SOFC-industry Chain

Materials → Cells → Integration module → System → Users

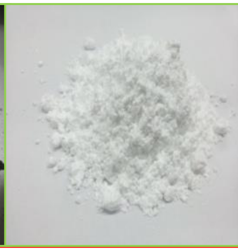


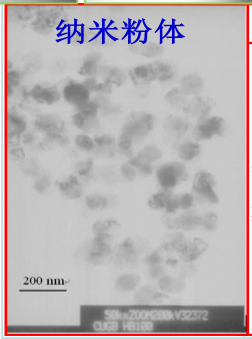
From powder to power

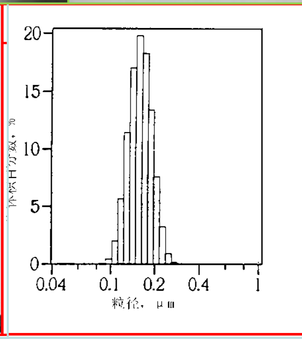
SOFC Key Materials

Electrolyte Materials

8YSZ $Ce_{0.8}Gd_{0.2}O_{2-\delta}$(GDC)
10ScSZ $Ce_{0.8}Sm_{0.2}O_{2-\delta}$(SDC)
10Sc1CeSZ $Ce_{0.8}Y_{0.2}O_{2-\delta}$(YDC)
$La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM)







Anode Materials

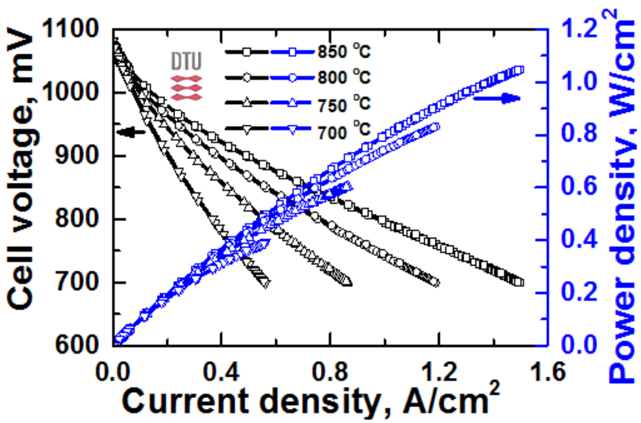
NiO/YSZ (50% YSZ by weight)
NiO/GDC (50% GDC by weight)

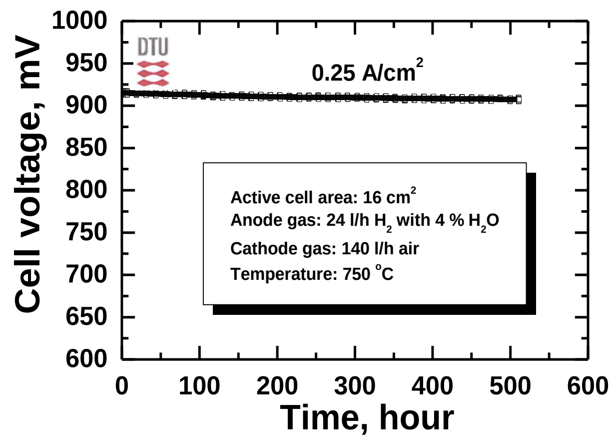
Cathode Material

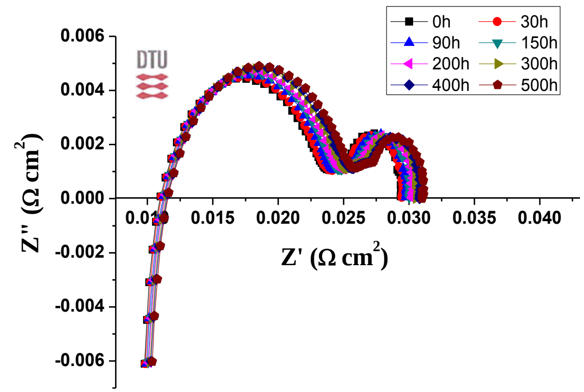
$(La_{0.8}Sr_{0.2})_{0.98}MnO_{3-\delta}$ (LSM) LSM/YSZ (50-50% by weight)
$La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ (LSCF) LSM/GDC (50-50% by weight)
$La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSC) LSCF/GDC (50-50% by weight)
$La_{0.8}Sr_{0.2}FeO_{3-\delta}$ (LSF) LSC/GDC (50-50% by weight)
$Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ (SSC) LSF/GDC (50-50% by weight)
SSC/GDC (50-50% by weight)

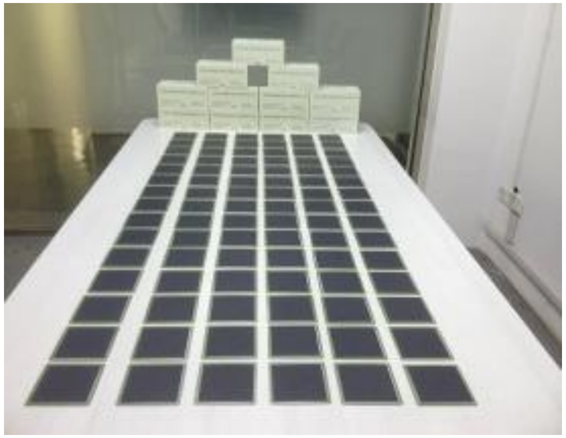
SOFC Components

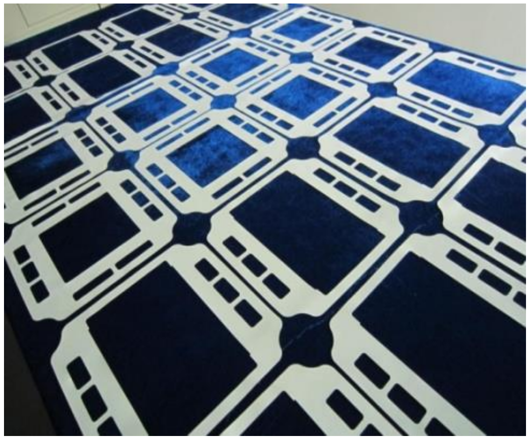
Electrochemical performance and durability of 10 ×10 cells









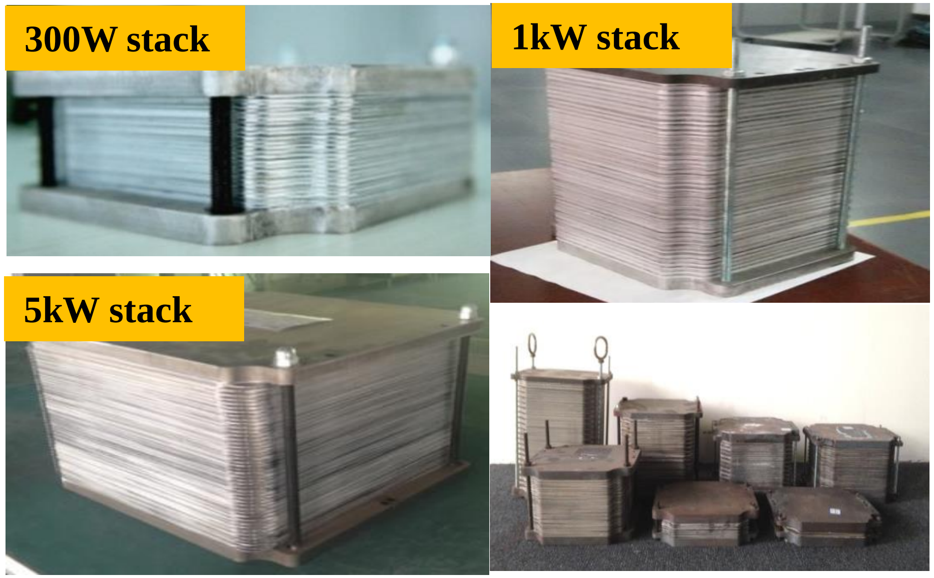


Single cell

Sealing

Interconnect

SOFC Integrated Modules

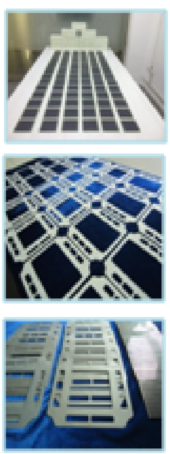


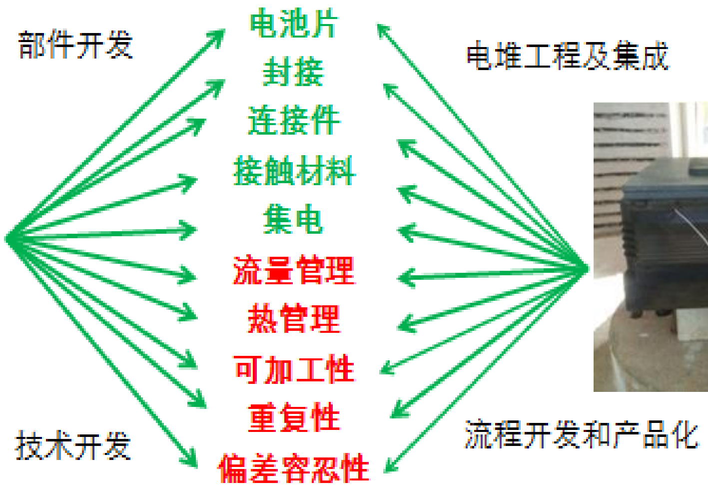
◆**Cutting-edge research**

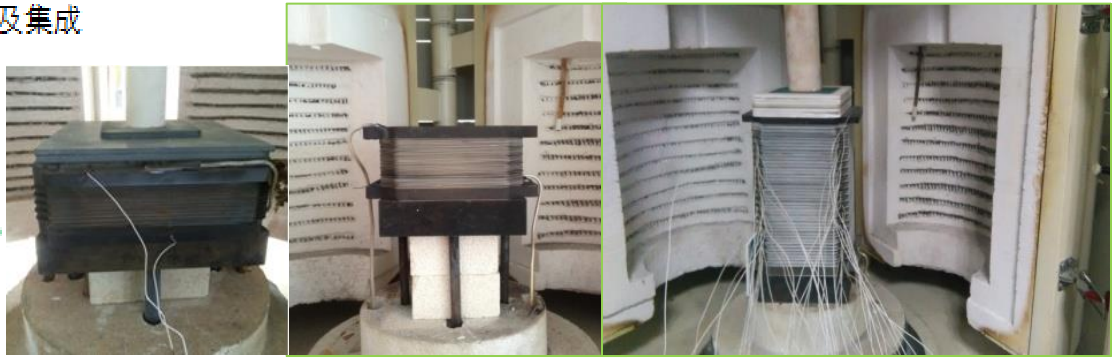
- Sealing material and technology
- Novel stack structure design
- Mult-field modeling and test
- Degradation factors and mechanism od stack
- 。。。

◆**Industry technology**

- Integrating technology——Know How
- Repeatability and reliability
- Standardization and modularization
- Characterization and test method
- Product standard
- 。。。



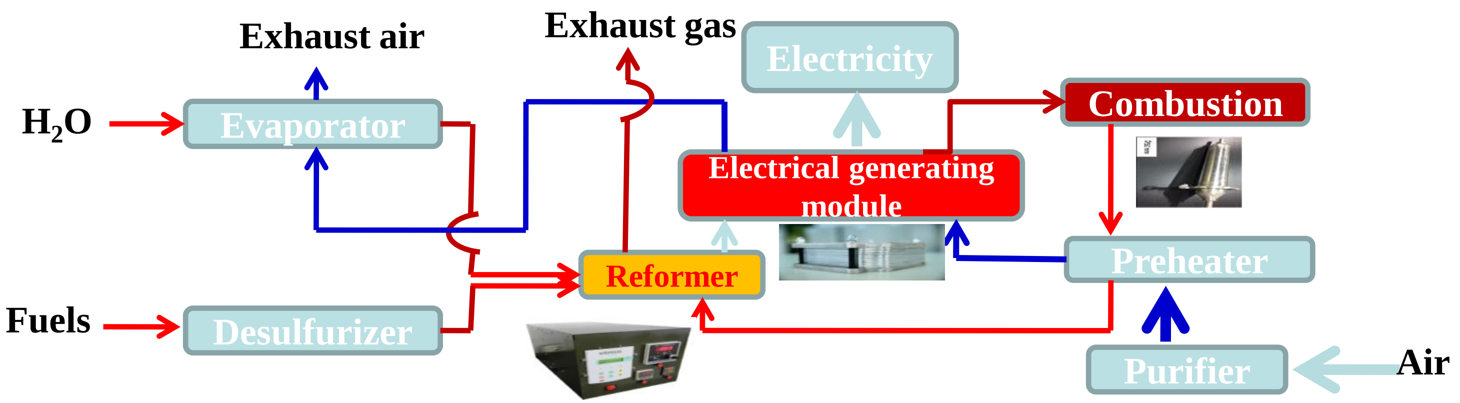




- **Establish standard packaging technology**
- **Realize mass production of stacks**

- **Integrating process of stack**

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℃-50℃

SOFC Demonstrations

The Beginning of SOFC Industry in China

◆**Suzhou Huatsing Jingkun Power Sysetm Co., Ltd:** Established in 2010, specialized in SOFC industrialization, have achieved substantially all of the SOFC technologies;

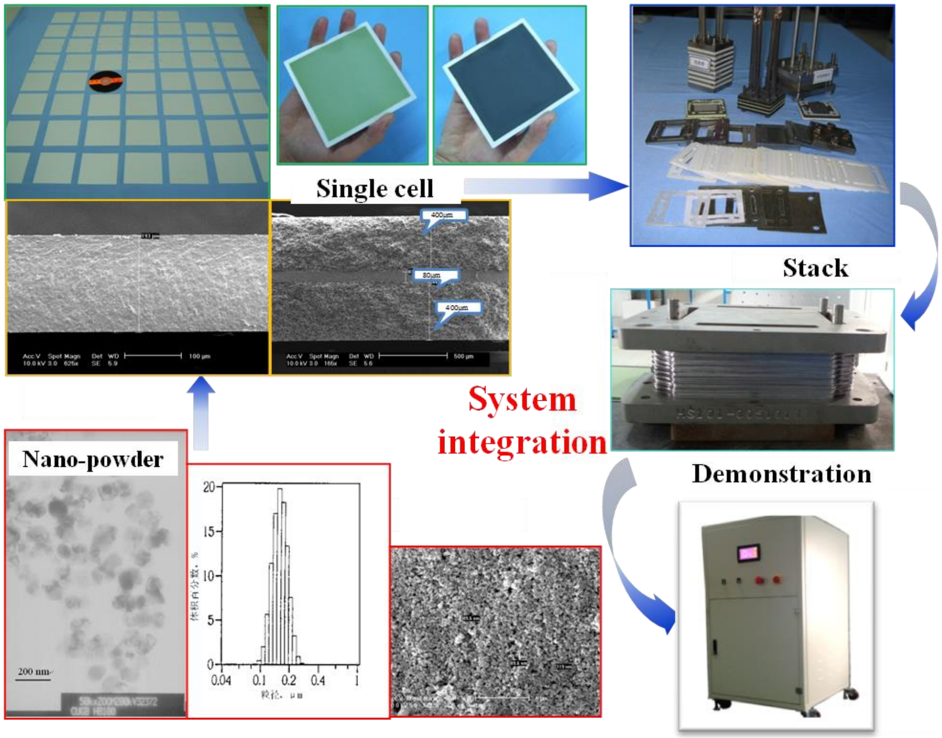
- January 2013, obtained 11 million venture capital;
- December 2014, demonstration and application of carbon-based fuel SOFC system (700 million);
- December 2015, obtained 200 million venture capital from Tsinghua for the manufacture and demonstration of SOFC power generation system.

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

◆ **G-cell Technonlogy Co.,Ltd.:** established by China University [illegible] 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.

苏州华清京昆新能源科技有限公司
Suzhou Huatsing Jingkun Power Sysetm Co., Ltd



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

苏州华清京昆新能源科技有限公司

Suzhou Huatsing Jingkun Power Sysetm Co., Ltd

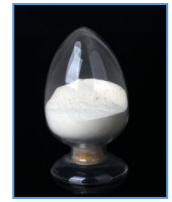
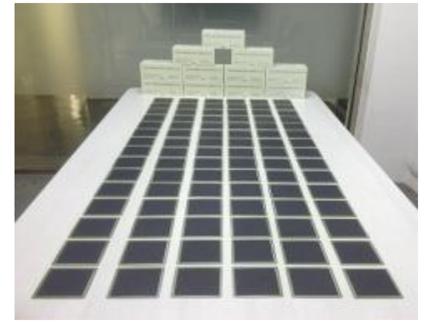
Founded in 2010

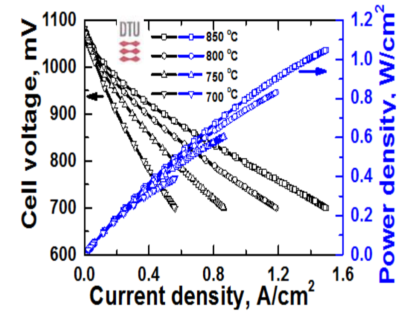
Cooperated with universities

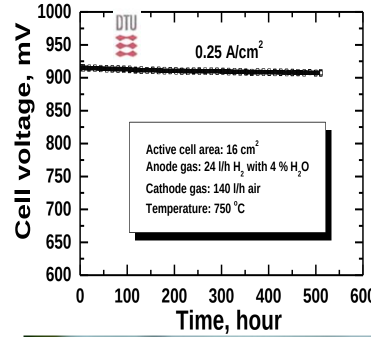
Undertaking national "973" project, and so on

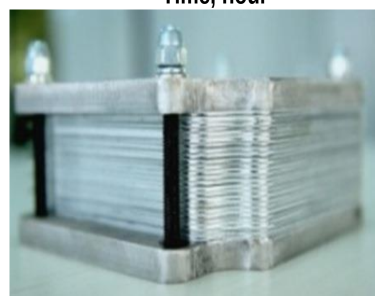
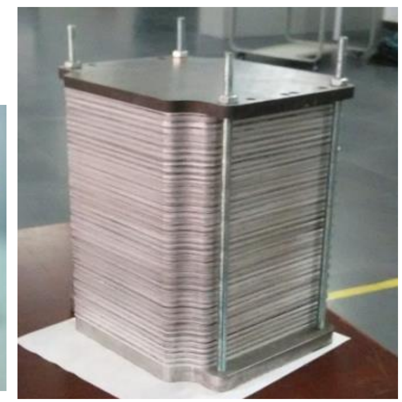
Put forward the SOFC industrialization in China

- **Materials**
- **Cells**
- **Integration module**
- **System**
- **Users**

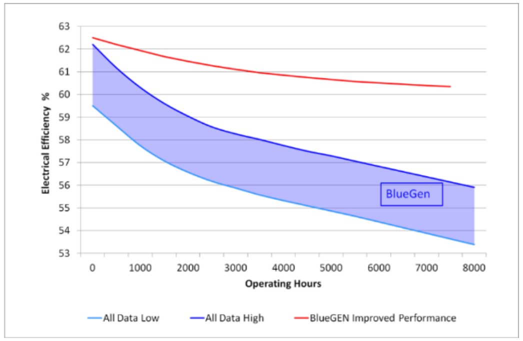





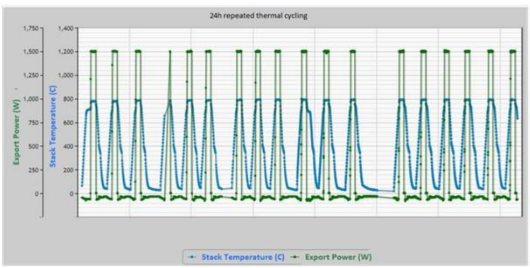


潮州三环(集团)股份有限公司
ChaoZhou Three-circle (Group) Co.,Ltd.



➢ Low degradation:

After 1 year operation at 750℃, electrical efficiency still over 60%. (Previous achievement by CFCL)



➢ Thermal cycle test:

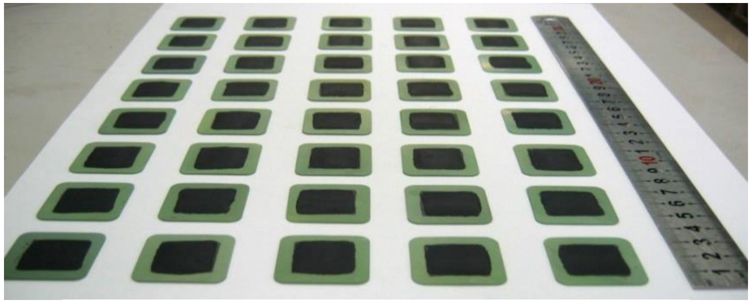
After 24 repeated thermal circle, average of 0.15% voltage degradation per cycle and without leakage. (Previous achievement by CFCL)

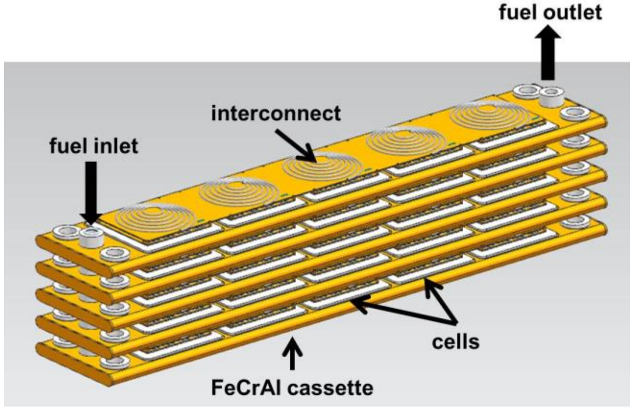
➢ Product name: C1 stack

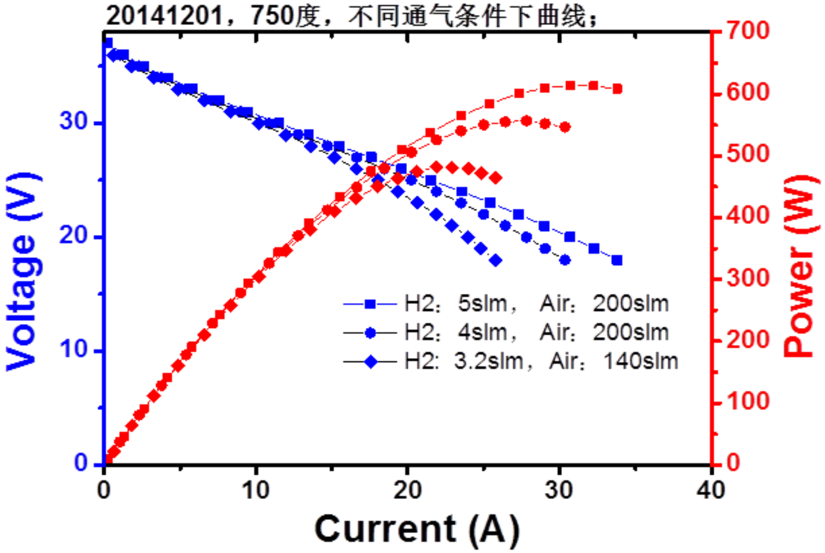
1. **1 kW power;**
2. **Stack efficiency degradation < 0.2%/khrs @ BlueGen system.**
3. **Stack DC electrical efficiency > 65% @ BlueGen system.**
4. **Thermal cycle resistance.**

吉世尔（合肥）能源科技有限公司
G-cell Technonlogy Co.,Ltd.

Founded in 2013





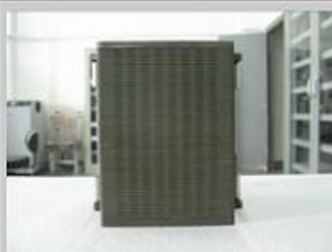
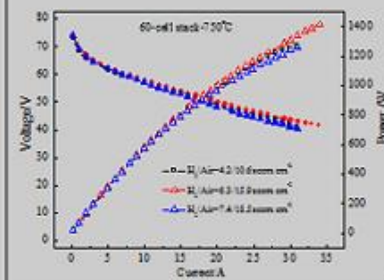


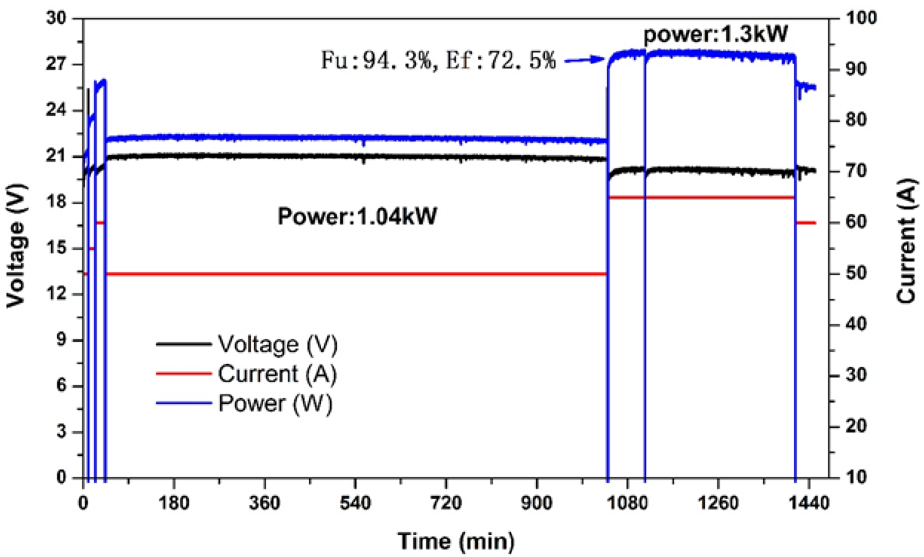
□Product name: C1 stack

1, 24V;

2, 1kW

宁波索福人能源技术有限公司
Ningbo SOFCMAN Energy Technology Co., Ltd.

SOFCMAN-A-Stack-601: 7.5kg;10cm×10cm×14cm	SOFCMAN-A-Stack-602: 8.5kg;10cm×10cm×78cm	SOFCMAN-A-Stack-601: 750℃ I-V curve
		
Price: 14,000RMB	Price: 15,000RMB	



Founded in 2014

➢ A stack module

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

Opportunities and Challenges of SOFC in China

- Suzhou Huatsing Jingkun Power Sysetm Co., Ltd
- ChaoZhou Three-circle (Group) Co.,Ltd.
- G-cell Technonlogy 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

IEA

Implementing Agreement *Advanced Fuel Cells*

Annex 32 – SOFC

THE YELLOW PAGES OF SOFC TECHNOLOGY

International Status of SOFC deployment

2015-2016

THANK YOU