Novel Electrodes for Low-Temperature SOFCs

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Outline

• Introduction
• Program Objectives
• Technical Approach
• Results to Date
  – Combustion CVD
  – In-situ potential dependent FTIR emission spectroscopy
  – Functionally Graded Electrodes

• Summary
• Future Work
Introduction: Electrode Processes

\[ 2e'(\text{electrode}) + V_{O}^{\text{electrolyte}} + \frac{1}{2}O_2(\text{gas}) \rightarrow O_O^X \]

- Ionization of \( O_{ad} \)
- Adsorption
- Diffusion
- Surface diffusion

E\textsuperscript{-} \hspace{2cm} e^-

\( O_{ad} \) \hspace{2cm} \( O_2 \)

Ionic and Electronic Transport

Electrolyte

Porous MIEC Electrode
Modeling of Porous MIEC Electrodes

- In the **Solid** MIEC

\[ J_k = -z_k F \left( \frac{u_k}{\tau_s} \right) [(1 - p)c_k] (\nabla \mu_k + z_k F \nabla \phi) \]

- Through the **Pores** of MIEC

\[ N_{O_2} = \left[ -\left( \frac{u_{O_2}}{\tau_g} \right) \nabla \mu_{O_2} + \nu \right] (p_{c_{O_2}}) \]

- At the **MIEC/O_2** Interface & TPBs

\[ J_V = J_{0,V} \left\{ \left( \frac{c_{V^*}}{c_V} \right) \exp \left( \frac{\alpha_a \Delta \mu_e}{RT} \right) - \left( \frac{p_{O_2}}{p_{O_2^*}} \right)^{\frac{1}{2}} \exp \left( \frac{\alpha_c \Delta \mu_e}{RT} \right) \right\} \]

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Distribution of Reaction Rate

Useful Thickness

$J_v$

CC  Porous MIEC  El.

TPB1

MIEC/O$_2$

CC  Porous MIEC  El.

TPB1

MIEC/O$_2$

TPB2
Objectives

• To develop highly efficient electrodes at low temperatures
  – Inexpensive metallic components may be used
  – Greater system reliability & longer optional life
  – Potential for mobile applications

• To develop simple and cost-effective processes for fabrication of electrodes with desired microstructures
Technical Approaches

- Rational design of functionally graded electrodes
- In-situ characterization of electrode processes using FTIR emission spectroscopy and impedance spectroscopy (IS)
- Investigating effect of geometry (TPB & surfaces) using micro-fabricated patterned electrodes
- Fabrication of electrodes by combustion CVD
Results to Date

- Nano-particles fabricated by combustion CVD and electrodes modified by CCVD
- In-situ pd-FTIR emission spectroscopy and IS
  - Cathode: mechanism of oxygen reduction
  - Anode: Sulfur tolerance and carbon deposition
- Functionally graded electrodes on extruded honeycomb cells
A Composite Electrodes

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Nano-Structured Electrodes
In-situ Characterization of SOFCs using pd-FTIR ES and IS

To understand elementary steps involved in electrode reactions in SOFCs;

To provide surface structural details under conditions for actual fuel cell operation; and

To rationalize the pd-FTIRES and Impedance spectra correlated to other data with the types of the intermediate species found at the functional interfaces.
Experimental Arrangements for Investigations into SOFC Reactions Using in-situ FTIR-ES, Raman, MS/GC, and IS

FTIR/Raman Accessory

Mass Flow Controllers

Argon

Fuel/O₂

Process Control System

Mass Spectrometer

Gas Chromatograph

Drier

Oxygen Sensor

Impedance Spectroscopy (IS)
Electroanalytical measurements

To Vent

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Optical Bench
for In-situ pd-FTIR Spectroscopy

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Optical Configuration for In-Situ pd-FTIR Emission Spectroscopy

Top: Oxygen Reduction
\[ \frac{1}{2}O_2 + V_o^{\ast} + 2e^- \rightarrow O_0^x \]

(\[ \frac{1}{2}O_2 + 2e^- \rightarrow O^2^- \])

Bottom: Oxygen Evolution
\[ O^{2-} - 2e^- \rightarrow 1/2O_2 \]

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Microstructure of The SSC/SDC Interface

Glycine-nitrate process:
- Cathode: Sm$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ (SSC)
- Electrolyte: Sm$_{0.2}$Ce$_{0.8}$O$_{1.9}$ (SDC)

A symmetrical cell: SSC/SDC/SSC
- Dry pressing SDC and screen-printing SSC

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Conditions for Spectra Collection

*In-Situ* pd-FTIR Emission Spectroscopy

To take the sample spectrum (Absorbance, \(-\lg(E/E_0)\))

To take the background spectrum \((E_0)\)

Do not need *blackbody* background.

By normalizing as \(E/E_0\) (%), the *greybody* emission (emission when no potential applied) is removed.
**Electrochemical Measurements**

*(Impedance and DC Performance)*

SSC/SDC/SSC, in 1% O\(_2\), at 550\(^\circ\)C

with DC bias, 0~1.1V with 0.2V increment

Controlled by charge transfer

\[
\frac{1}{2} O_2 + \{V^-_O + 2e'\} \rightarrow O^X_O
\]
Possible Elementary steps/Reaction pathways

\[ \frac{1}{2} O_{2,\text{gas}} \xrightarrow{\text{des}} \frac{1}{2} \left\{ O_{2,\text{ad}} \xrightarrow{\text{diss}} O_{\text{ad}} \xrightarrow{+e'} O^-_{\text{ad}} \right\} \xrightarrow{+e'} O_{\text{ad}} \xrightarrow{-e'} O^-_{\text{ad}} \xrightarrow{+e'} 2O^-_{\text{ad}} \xrightarrow{+(V_{\text{O}}+e')} O^X_{\text{O}} \xrightarrow{-(V_{\text{O}}+e')} O^X_{\text{O}} \]

Charge Transfer Steps

\[ O_{2,\text{ad}} + e' \rightarrow O^{-}_{2,\text{ad}} \]
\[ O^{-}_{2,\text{ad}} + e' \rightarrow O^{-}_{2,\text{ad}} \rightarrow O^{-}_{\text{ad}} \]
\[ O^{-}_{\text{ad}} + e' \rightarrow O^{-} \]

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In-Situ pd-FTIRES Spectra

Comparison of pd-FTIRE spectra for three different feed gas conditions: (a) air, (b) 1% O₂ in N₂, and (c) N₂.

Dashed lines indicate cubic fit to baseline. Electrochemical characteristics are listed in Table 1.
In-Situ Pd-FTIRES Spectra - After local baseline correction

(a) In air (η: 0 to 320 mV)
(b) In 1%O₂ (η: 0 to 760 mV)
(c) In N₂ (η: 0 to 690 mV)

After local baseline correction
Peak Heights v.s. DC Overpotential

(a) in 1% O$_2$
- 1236 cm$^{-1}$, perturbed O$_2^-$
- 1123 cm$^{-1}$, O$_2^-$
- 930 cm$^{-1}$, O$_2^{2-}$

(b) in N$_2$
Effect of mass transfer observed at high overpotentials
Proposed Reaction Mechanism for Oxygen Reduction

Rate-determining step (rds): $\text{O}_{2,\text{ad}}^– + e' \rightarrow \text{O}_{2,\text{ad}}^{\equiv}$
Evolution of Oxygen - SSC/SDC/SSC, in 1% O₂ at 500°C

550 °C, with DC bias

0 ~ 1.1V, with 0.2V increment

0 ~ -1.1V, with -0.2V increment

ΔE/E₀ (%) vs. Wavenumber/cm⁻¹
SSC: Sm_{0.5}Sr_{0.5}CoO_{3-δ}

LSC: La_{0.6}Sr_{0.4}CoO_{3-δ}

LSCF: La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ}

LSF: La_{0.6}Sr_{0.4}FeO_{3-δ}

SDC: Sm_{0.2}Ce_{0.8}O_{1.9}
In-situ FTIRES – Anodes in SOFCs

**H₂ as background and CH₄ as sample**

**After 5 min in CH₄**

- 2143 cm⁻¹: CO (Adsorbed)
- 1712 and 1540 cm⁻¹: Graphite
- 1070-800 cm⁻¹: Metal (Ni or Cu) carbonato (CO₃) complexes

**CH₄(gas)**

**Ni-SDC Anode**

**Cu-SDC Anode**
Ni-CeO$_2$ Based Anodes

[Graphs and tables showing experimental data related to Ni-CeO$_2$ anodes, including Faraday (torr) vs. time, and FTIR spectra with wavenumbers and wavenumber per cm$^{-1}$ data.]
Cu-CeO$_2$ Based Anodes

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SUMMARY – FTIR Studies

• A strong adsorption band at 1124 cm\(^{-1}\) (\(O_2^-\)), two weak adsorption bands at 1236 cm\(^{-1}\) (perturbed \(O_2^-\)) and 930 cm\(^{-1}\) (\(O_2^{2-}\)) were observed on oxygen reduction.

• The rds is the charge transfer step, \(O_{2,\text{ad}}^- + e' \rightarrow O_{2,\text{ad}}^{\text{=}2}\)

• Broad spectral features (baseline shifts), infrared electro-emission effect, is induced by electrochemical polarization.

• The emission difference spectra of Ni-SDC and Cu-SDC cermet anodes at 550\(^{\circ}\)C unveiled the nature of intermediate species when methane was used as the fuel. Graphite peaks were found at 1712 and 1540 cm\(^{-1}\). The broad bands at 1070-800 cm\(^{-1}\) were possibly metal (Ni or Cu) carbonato (\(CO_3\)) complexes.
Functionally Graded Electrodes on Honeycomb Cells
Hybrid Metal/Electrolyte Monolithic Low Temperature SOFCs
Electrode Processing

- Extruded honeycomb
- Slurry coating
- Drying, Sintering
- Honeycomb fuel cell

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Cathode for YSZ Fuel Cells

- **LSM-YSZ**
  - Efficient performance above 800°C
  - 1.31 Ωcm⁻² at 750°C
  - E. Murray, solid state Ionics 2001

- **LSM-GDC**
  - Improved performance below 800°C
  - 0.49 Ωcm⁻² at 750°C
  - E. Murray, solid state Ionics 2001

- **Graded composites of LSM-LSC**
  - Much better performance
  - 0.2 Ωcm⁻² at 750°C
  - NT Hart, J. Power sources 2002
Functionally Graded Electrodes

Interfacial resistance ($\Omega \text{cm}^2$) vs. Temperature ($^\circ\text{C}$)

YSZ | GDC | LSM | LSCF
--- | --- | --- | ---
1 | 2 | 3 | 4 | 5

Graph showing the interfacial resistance in different graded electrode samples at various temperatures.
Sample 5: LSM/GDC/LSCF

- LSCF
- LSCF50+GDC50
- LSM25+LSCF25+GDC50
- LSM50+GDC50
- YSZ

30.0 μm
IS for Graded Electrodes

Fired at 1100 °C, measured in air
Fired at 1100 ºC, tested at 800 ºC
Cathodes for YSZ Honeycomb Fuel Cells

Graded cathode, Hart, JPS 106(2002)42
LSM-GDC cathode, Murray, SSI 143(2001)265
Graded cathode

Interfacial resistance, $\Omega \text{cm}^2$

Temperature, 1000/T

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Electrodes of High-Catalytic Activities

- High catalytic properties for oxygen reduction
- High catalytic properties for direct oxidation of hydrocarbon fuels or reforming of hydrocarbon fuels
Comparison of a new cathode and a cathode graded in composition
Cathodes for Zirconia Fuel Cells

Interfacial resistance, $\Omega \text{cm}^2$

Temperature, $1000/T$

- Graded cathode, Hart, JPS 106(2002)42
- LSM-GDC cathode, Murray, SSI 143(2001)265
- Graded cathode
- YDB cathode

One Order of Magnitude

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Effect of Firing Temperature/Thickness - Measured at 600°C

Fired at 750°C/2 hrs

Fired at 850°C/2 hrs

Rp can be further reduced by microstructure optimization
Summary - Electrode Development

• Cathodes graded in composition show interfacial resistances about 10 times lower than that of a conventional LSM-YSZ cathode;

• The performances are dependent on the microstructures, and is favored by low-temperature sintering;

• Interfacial resistance of graded cathodes as low as 0.47 $\Omega \text{cm}^2$ was achieved at 750$^\circ$C. However, it increased to 4.1 $\Omega \text{cm}^2$ at 600$^\circ$C;

• A new cathode showed much lower interfacial resistances than the graded cathodes, 0.30 $\Omega \text{cm}^2$ at 600$^\circ$C, about 10 times better; and

• High performance: >600 mW/cm$^2$ at 600$^\circ$C
Future Work

• Mathematical Modeling of Functionally Graded Electrodes
  → The Best design

• In-situ pd-FTIRES, IS, and MS
  → High Catalytic Activity for fast reactions
    – Cathode: Mechanism of oxygen reduction
    – Anode: Sulfur tolerance and carbon deposition

• Patterned electrodes
  → Optimal Architecture for Rapid Mass Transport

• Combustion CVD → Nano-Structure