B1.3: Composite Cathodes for Intermediate Temperature SOFCs: A Comprehensive Approach to Designing Materials for Superior Functionality

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**Concept**

- Solid Oxide Fuel Cells are to be used as power generators on the Moon or Mars, or as back up generators when wind or solar power are not available.
- If used in reverse, SOFCs could serve as a source of oxygen by water electrolysis.
- We are going to produce single element SOFCs using cathodes with complex composite structures which will enhance SOFC performance. The ultimate goal of the proposed research is to design, manufacture and demonstrate the SOFC stack that efficiently operate at 750-800°C.
- NASA will benefit by using efficient energy generating device in the space.

**Application**

- O + 2ē → O²⁻  
  Determine:  
  Surface adsorption sites  
  Adsorbed species – O²⁻, O²⁻, O²⁻, O₂²⁻, O₂⁻, O³⁻

**Technical Approach**

- A schematic presentation of the three types of the dense SOFC cathodes deposited by RF magnetron sputtering on the 10mol%Sc₂O₃-1mol%CeO₂-ZrO₂ electrolyte.

**Collaborations & Leveraging**

- **PI** - Nina Orlovskaya, **Co-PIs** - Ahmad Sleiti, Jay Kapat, Artem Masunov, Ratan Guha,
- **PhD Students** – Deanna Altilio, Nicholas Bernier, Arun Kumar Menon, Rangan Majumdar, Jaruwan Mesit, Shruba Gangopadhyay
- **Industry collaborators** – Nextech Materials, Scribner, Air Products and Chemicals, Siemens
- **NASA contact** - Narottam P. Bansal, NASA GRC
- Two NSF proposals pending - $540,000  
  One PRF proposal pending $150,000  
  Air Products and Chemicals pending - $50,000

**Fig. 2.** Three types of the SOFC cathodes: a) porous single phase electronically conductive oxides; b) porous single phase mixed ionic electronic conducting oxides; c) porous two phase composite cathodes.

**Fig. 3.** A schematic presentation of the three types of the dense SOFC cathodes deposited by RF magnetron sputtering on the 10mol%Sc₂O₃-1mol%CeO₂-ZrO₂ electrolyte.

**Fig. 4.** An example of the electron beam etching techniques. Focus laser beam (flu). 

**Electrolyte**

- Gd₀.₂Ce₀.₈O₂, La₀.₇Sr₀.₃MnO₃,
- (La₀.₇Sr₀.₃)₀.₉₈MnO₃,
- La₀.₆Sr₀.₄Fe₀.₈Co₀.₂O₂,
- Ba₀.₅Sr₀.₅Co₀.₈Fe₀.₂O₃

**Electrode**

- O₂⁻, O₂⁻, O²⁻, O₂⁻, O²⁻, O³⁻
Objectives

The goal of this research is to develop and probe the electrochemically active composite cathode surfaces and interfaces for Intermediate Temperature SOFCs by in-situ Raman and impedance spectroscopy in parallel with ex-situ X-ray diffraction (XRD) to determine the oxygen reduction and possible instability and degradation mechanisms as a function of the cathode’s structural (composition, density, grain size, pore structure) parameters. Analytical models describing the performance of IT SOFC composite cathodes will be developed and verified.
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Tasks

- Fabricate series of cathode/electrolyte structures in which the key cathode variables are systematically varied.
- Develop an in-situ spectroelectrochemical Raman cell to probe surface catalytic mechanisms and dynamics as a function of cathode variables, temperature, oxygen partial pressure, applied voltage, and current.
- Develop robust cell fixture and assembly hardware for half-cell and symmetric-cell SOFC electrochemical testing and evaluation that will enable the characterization of the materials before, during, and after extended operation.
- Measure the simultaneous impact of the cathode and environmental variables on transport mechanisms and dynamics with impedance spectrometry.
- Study of cathode/electrolyte interfaces and cathode surfaces by in-situ Raman and impedance spectroscopy and I-V characterization as well as by XRD analysis.
Operating principles of SOFC

The cell may be supported by anode, cathode, electrolyte or special materials.

The cell geometry may be planar, tubular, flattened tubes or .......

Only imagination put limits on the cell design.

Similar, a wealth of stack designs exists.
Advantages of SOFC

- Operate at elevated temperatures

→ **possibility of catalytic conversion of practical fuels directly within fuel cell** - no complex, expensive external catalytic fuel processor

  **Internal reforming**

→ Reduced complexity

→ Higher efficiency through improved heat utilisation

→ **Flexibility in choice of fuel**
  - High efficiency through production of high grade heat
  - Tolerant to CO
  - Greater tolerance to impurities, including sulphur, than other fuel cells
  - No precious metals

SOFC operating temperatures:
900-1000°C – High Temp SOFC
600-800°C - Intermediate Temp SOFC
500-600°C – Low Temp SOFC

Schematic of processes occurring within the air electrode, electrolyte and fuel electrode and at their interfaces, superimposed upon an appropriate microstructure for such an electrode/electrolyte structure.

Starting Point
Oxygen reduction on the porous LaSrMnO$_3$ cathode

**LIMITING STEPS**

1. Gas diffusion
2. Adsorption
3. Charge transfer reaction (1)
4. Surface diffusion
5. Charge transfer reaction (2)
6. Incorporation of oxygen ions into electrolyte lattice

\[
\begin{align*}
O_2(\text{bulk}) & \rightarrow O_2(\text{interface}) \\
O_2(\text{interface}) & \rightarrow 2O_{\text{ad}} \\
O_{\text{ad}} + e^- & \rightarrow O^-_{\text{ad}} \\
O^-_{\text{ad}} & \rightarrow O^-_{\text{TPB}} \\
O^-_{\text{TPB}} + e^- & \rightarrow O^{2-}_{\text{TPB}} \\
O^{2-}_{\text{TPB, LSM}} + V_{O, YSZ} & \Rightarrow O^x_{O, YSZ}
\end{align*}
\]

At high temperatures $>900^\circ$C YSZ and LSM can react to form pyrochlore La$_2$Zr$_2$O$_7$ or/and perovskite SrZrO$_3$

High Performance Cathodes

The LSFC perovskite increases the ionic and electronic conductivity and the surface exchange of oxygen, which is explained by the larger number of oxygen vacancies and electronic holes. It was reported that the measures current densities of cells with A site deficient cathode LSCF were as high as 1.76 A cm\(^{-1}\) at 800\(^\circ\)C and 0.7V, which is about twice the current density of cells with LaSrMnO\(_3\)/YSZ composite cathodes. The addition of GDC to LSFC results in even lower polarization resistance – 0.07 \(\Omega\) cm\(^2\) at 800\(^\circ\)C, 0.11 \(\Omega\) cm\(^2\) at 750\(^\circ\)C and 0.22 \(\Omega\) cm\(^2\) at 700\(^\circ\)C.
Oxygen reaction pathway and extension of active site from TPB to the electrode surface and to electrode/electrolyte boundary

Elementary steps:
1) Gas diffusion
2) Adsorption
3) Dissociation
4a) Surface diffusion
4b) Bulk diffusion
5a) Ion transfer at TPB
5b) Ion transfer at the electrode surface
5c) Ion transfer at the electrode/electrolyte boundary

Kawada, Solid State Ionics, 2006
Concept – In-situ environmental Raman stages

Raman spectra of LaSrMnO$_3$ thin film with and without AFM tip enhancement
Application

As we venture farther and farther from the surface of our own planet, one of our major limiting factors will always be our source of energy. For any future off-planet base that we set up, whether it be in orbit around the earth, on the moon, or even on Mars, a reliable long term power supply is one the first issues that needs to be addressed.

SOFC - Ideal device for localized and remote applications - especially Combined Heat and Power (CHP) – NASA Application
Manufacturing Button Cells

- Tape Casting
- Sintering
- Three Roll Mill
- Completed Button Cell
- Screen Printing
- Finished Inks
SEM of Complete Button Praxair Cell

LSFC+GDC Cathode

NiO+ScCeZrO$_2$ Anode
Figure 1. a) A linear shrinkage of LaMnO$_3$; (La$_{0.7}$Sr$_{0.3}$)$_{0.98}$MnO$_3$; La$_{0.6}$Sr$_{0.4}$Fe$_{0.8}$Co$_{0.2}$O$_3$; Gd$_{0.2}$Ce$_{0.8}$O$_{2-\delta}$ single phase ceramics, b) A linear shrinkage of three composite ceramics.

2. a) Porosity of LaMnO$_3$; (La$_{0.7}$Sr$_{0.3}$)$_{0.98}$MnO$_3$; La$_{0.6}$Sr$_{0.4}$Fe$_{0.8}$Co$_{0.2}$O$_3$; Gd$_{0.2}$Ce$_{0.8}$O$_{2-\delta}$ single phase ceramics, b) Porosity of three composite ceramics.
Lattice Parameters of perovskite/fluorite cathode samples

Unit cell volume of perovskite and fluorite phases as a function of sintering temperature of:

a) LaMnO$_3$, b) (La$_{0.7}$Sr$_{0.3}$)$_{0.98}$MnO$_3$, c) La$_{0.6}$Sr$_{0.4}$Fe$_{0.8}$Co$_{0.2}$O$_3$, d) Gd$_{0.2}$Ce$_{0.8}$Ob$_{\delta}$. 
Lattice Parameters of perovskite/fluorite cathode samples

Raman spectra (633nm He-Ne laser) of LaMnO$_{3}$-CeO$_{2}$ nanopowders synthesized by Pechini method and calcined at 700°C. The insert shows the LaMnO$_{3}$-CeO$_{2}$ nanopowders micrograph by SEM.
Before and After SEM of DKKK Cell

Anode

Cathode

Cathode

After Testing

Anode
Test Results

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![Graph showing current vs. voltage and power density](image)

- **Current (amps)** vs. **Voltage (volts)**
- **Power Density (mW/cm²)**
A schematic presentation of the three types of the dense SOFC cathodes deposited by RF magnetron sputtering on the 10mol%Sc$_2$O$_3$-1mol%CeO$_2$-ZrO$_2$ electrolyte substrates.

Dense Electronic Conductor Cathode

Dense Mixed Conductor Cathode

Dense Composite Cathode

The electrode patterning using lithographic or ion beam etching techniques. Focused Ion Beam (FIB) will be also used to pattern nanosized porosity in the controllable manners.
Modeling Planar SOFC

- CFD modeling of the cathode performance.
- Experimental verification and validation of the models

**FLUENT SOFC**

- Local electrochemical reactions coupling the electric field and the mass, species, and energy transport.
- Electric field solution in all porous and solid cell components, including ohmic heating in the bulk material.
Cluster Computing

- # Nodes: 48 (Sun Fire V20z)
- CPU: Dual AMD Opteron 242
  - 1.6GHz processors
- Memory: 2 GB
  - (6GB in 8 Nodes)
- Network: Gigabit Ethernet
- Disk: 2 x 36 GB in each node
- OS: SunOS 5.9, Linux
- Software:
  - Car-Parrinello Molecular Dynamics (CPMD)
  - Fluent, gcc, JDK 1.5, MPICH, mpiJava, JPVM, POSIX thread
  - OMPi OpenMP, VCluster
Collaborations

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