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Materials Issues and Experiments for HTE and SO_3 Electrolysis

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Project #PDP30

U.S. Department of Energy

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High Temperature Steam Electrolysis Stack Post-test Evaluation and Electrode Development

Overview

Timeline

- Project start – FY'04

Budget

- FY06 - $583k
- FY07 - $344k

Barriers

- Stack degradation
- Electrode performance and durability

Argonne contributors

Ann Call, Jeremy Kropf,

Victor Maroni, and Deborah Myers

Partners

- Idaho National Laboratory
- Ceramatec, Inc.

Objectives

1) Determine causes of degradation in stack components from 25-cell (1000 h) and 22-cell (200 h) stack tests

2) Develop oxygen and steam-hydrogen electrodes that show significantly improved area specific resistance and durability over state-of-the-art electrodes.

Approach

1) **Post-test stack evaluation:**
   - **Map cell and bipolar plate surfaces to find sources of degradation using:**
     - ***4-point resistivity***
     - ***X-ray fluorescence from Advanced Photon Source***
     - ***Raman-microspectroscopy***
   - **Use mapping results and analyze selected cross sections with Scanning Electron Microscopy**

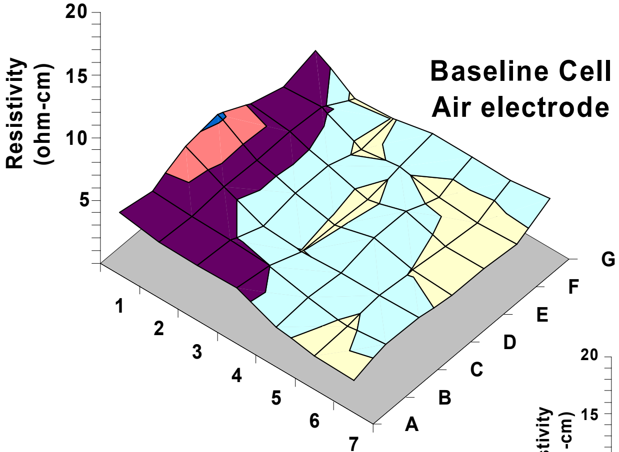
2) **Improved oxygen and steam/hydrogen electrodes**
   - **Pr_2NiO_4 - polarization, stability tests**
   - **$La_{1-x}Sr_xMn_{1-x}B_xO_3$ B= Cr, Al, Ga – polarization, stability tests**

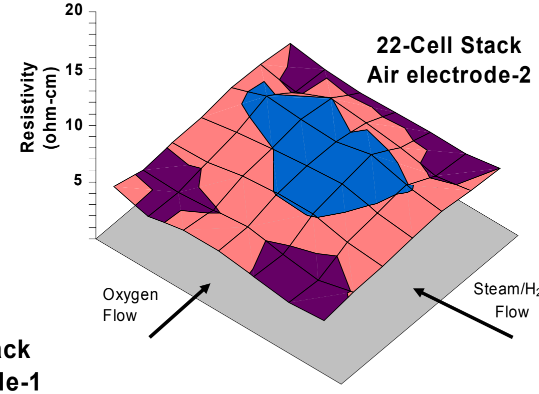
Resistivity maps for oxygen electrodes show degradation at hydrogen exit of cell

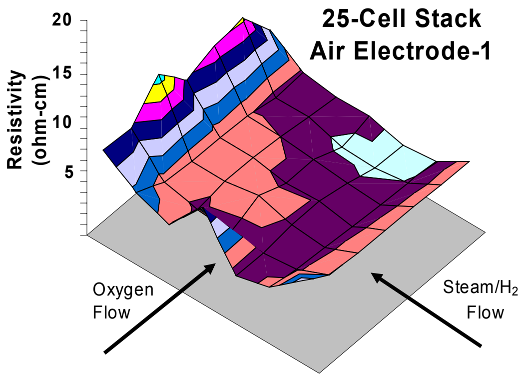
- Baseline Cell (untested) reasonably flat resistivity. 2-6 ohm-cm

- 22-cell stack (200-h) higher resistivity but reasonably flat. 3-7 ohm-cm

- 25-cell stack (1000-h) large growth in resistivity toward hydrogen/steam exit of the cell. 11 – 12 ohm-cm

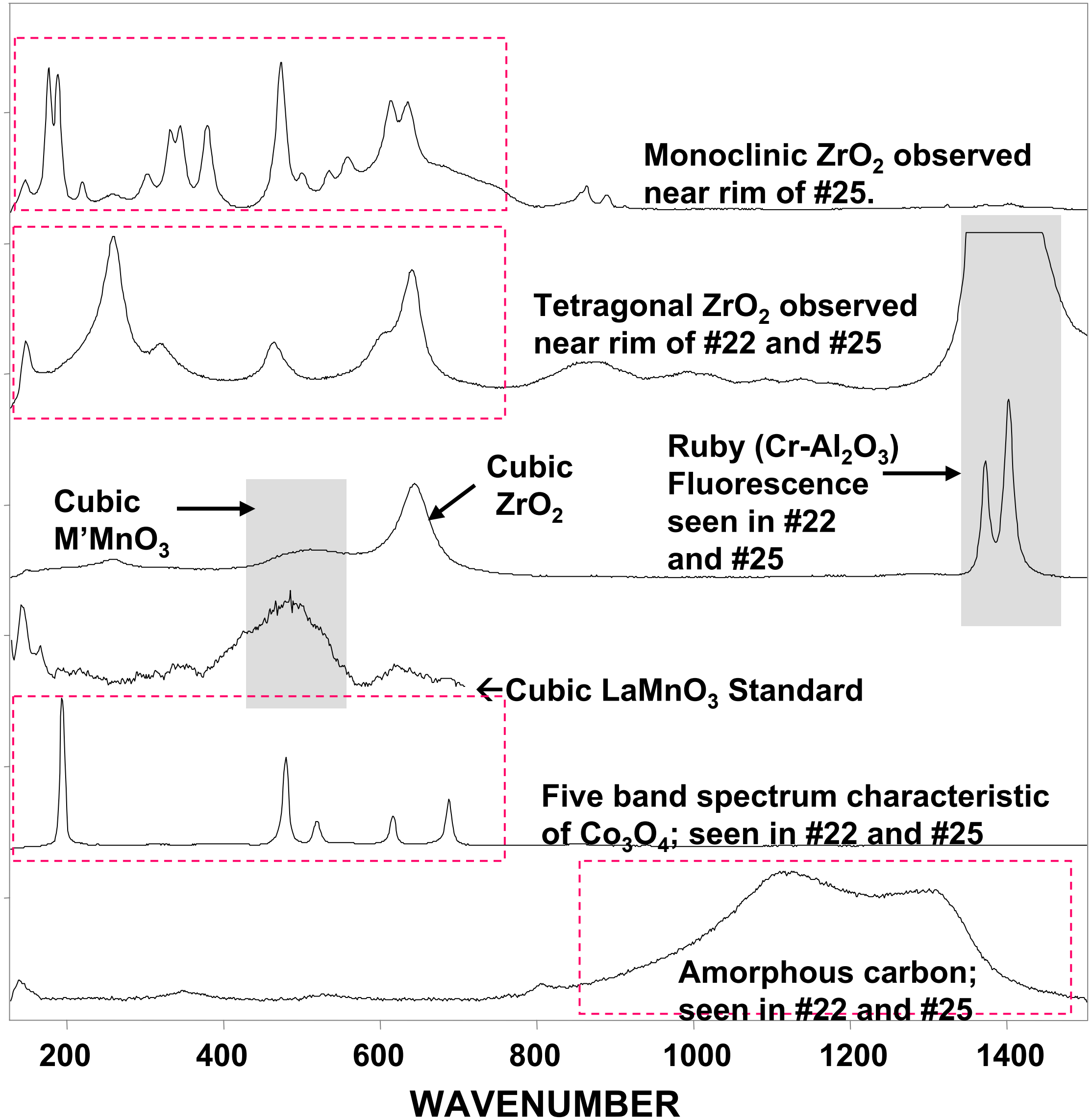






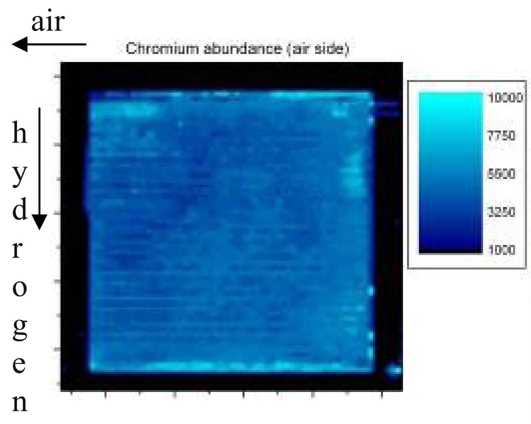
Raman micro-spectroscopy on oxygen electrodes identifies unexpected phases

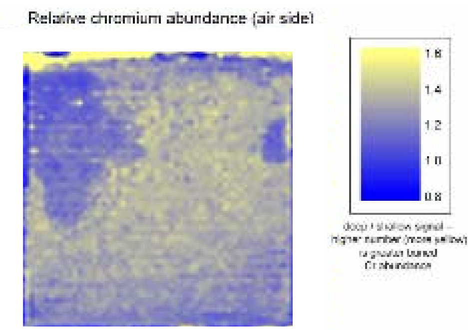
- Monoclinic zirconia observed on exposed edges of the ScSZ plate
- Chromium reacted with Al in sealant near edge of electrode

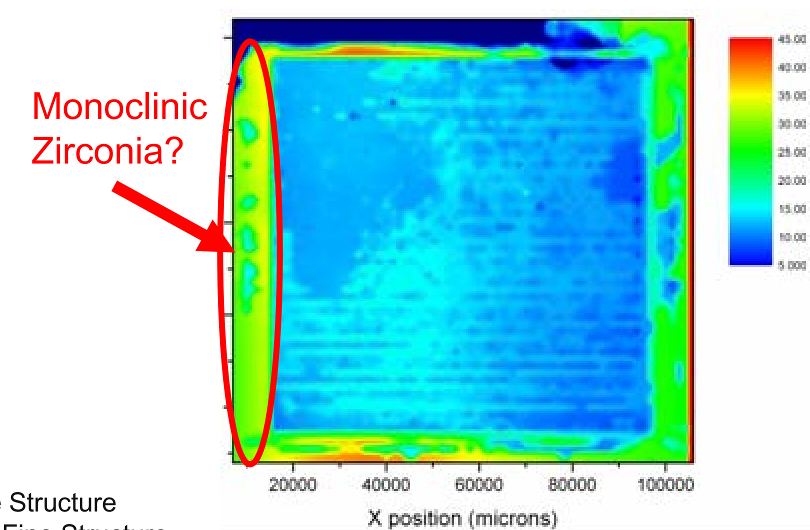


X-ray fluorescence and transmission show Cr migration and thickness variations in the cell

- Cr deposits along edges of sealant
- Cr deposited only in electrode region and not on zirconia $\Rightarrow$ solid state diffusion
- Gas flow direction is evident by Cr-deposition pattern
- Cr has migrated into the electrode towards electrolyte interface
- Thickness variation in electrode
- Increased transmission near known degraded edge
- Increased transmission near oxygen seal
- Would like to use XANES & EXAFS determine **chemical state of elements** in areas of interest

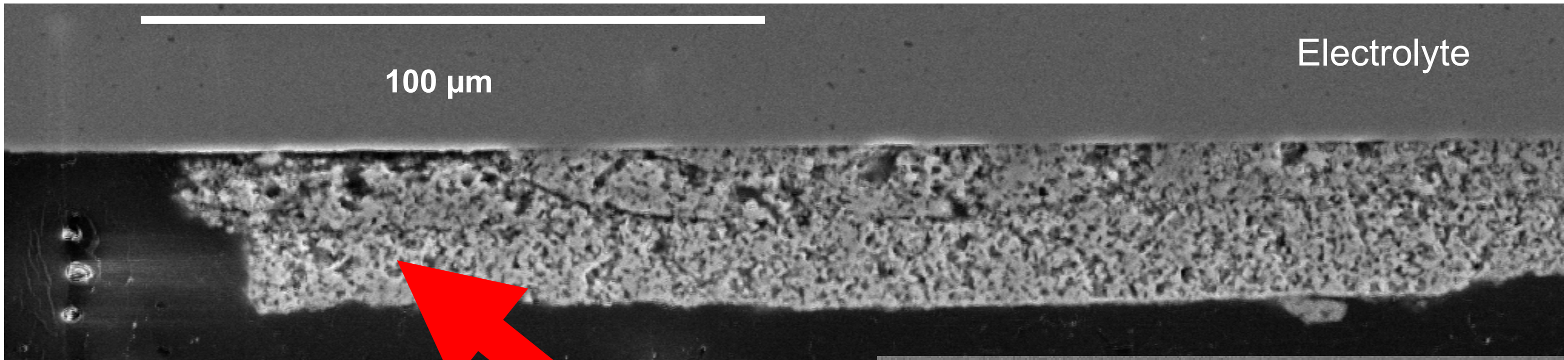


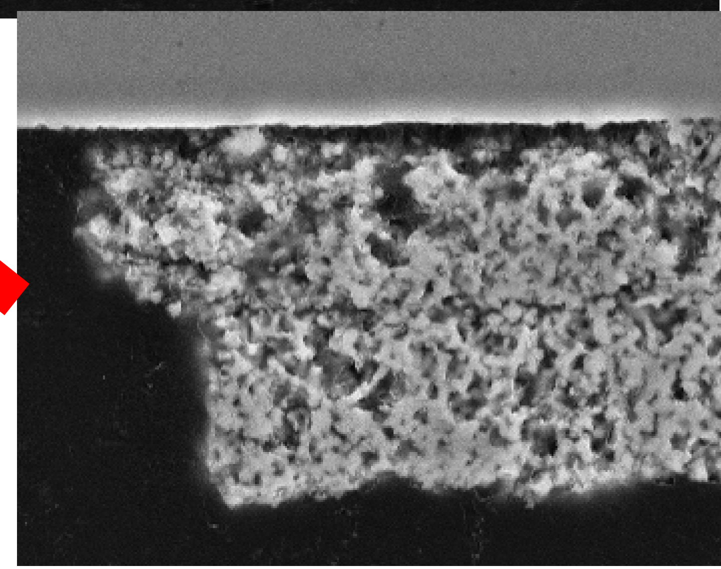




XANES: X-ray Absorption Near Edge Structure
EXAFS: Extended X-Ray Absorption Fine Structure

SEM analysis of oxygen electrode shows delamination in the oxygen electrode

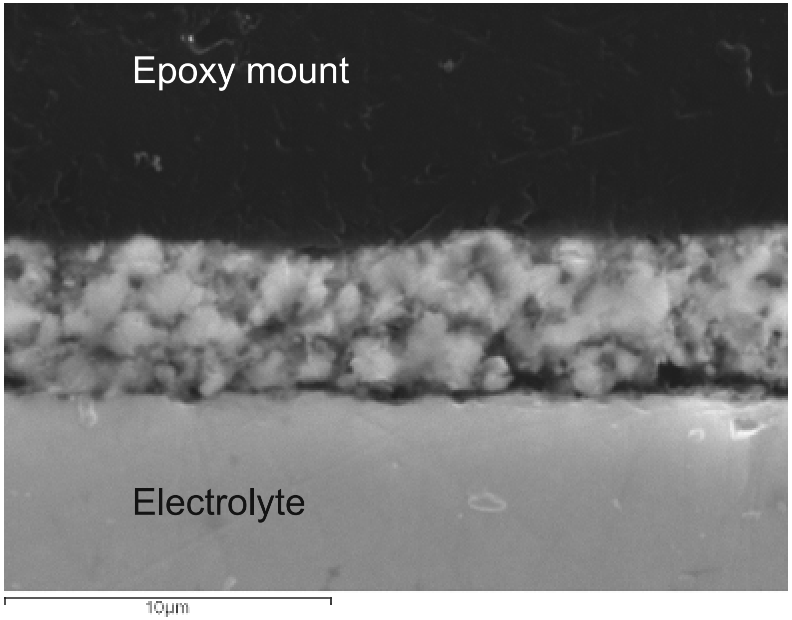




- **Delamination near the edge of the oxygen electrode was found where high resistance was measured with the 4-point probe**
- **Internal defaults were also seen near the edge**

SEM analysis of steam-hydrogen electrode identifies Si and Al contamination

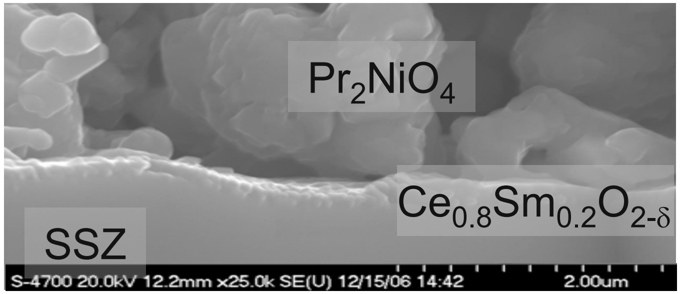
- **Area with low resistivity on 4-point probe maps:**
  - **Al present at electrode/bond layer interface**
  - **More Al near the sealed edge (Al:Ce = 0.05 – 0.25)**
- **Area with high resistivity on 4-point probe maps (at the edge):**
  - **More Si found near where bond layer was removed (Si:Ce = 0.05 – 0.24)**
  - **Al found throughout (Al:Ce = 0.16 – 0.29)**

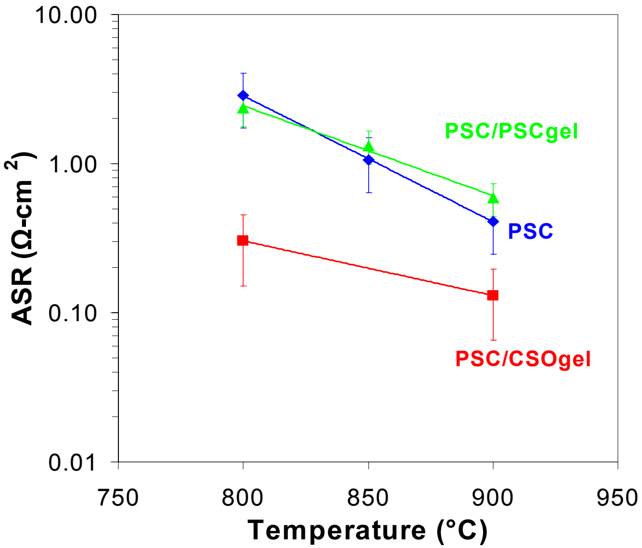


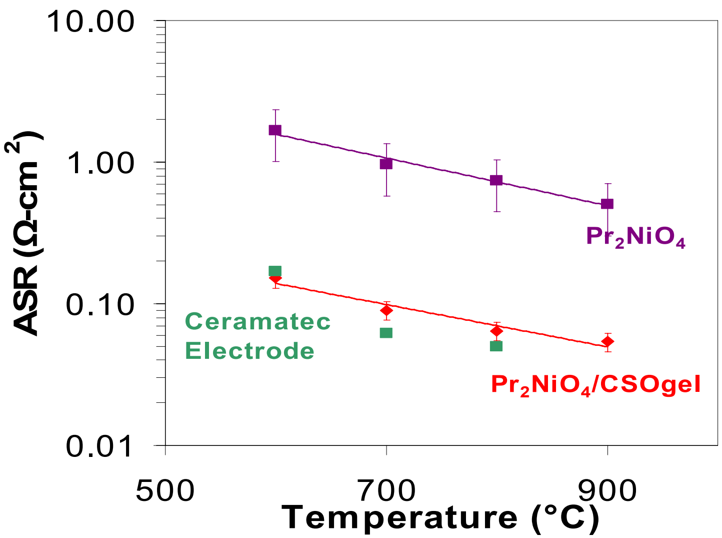
- **Increased contaminants near the sealed edges indicate that the seal material may be the source of Si and Al**

High temperature electrolysis oxygen electrodes improve with CSO interlayer

- Addition of a CSO interlayer improves performance of PSC electrodes
  - No secondary phases found by XRD
- CSO interlayers improve the performance of Pr_2NiO_4
- The roughness on the top of the ceria layer may contribute to the improved performance



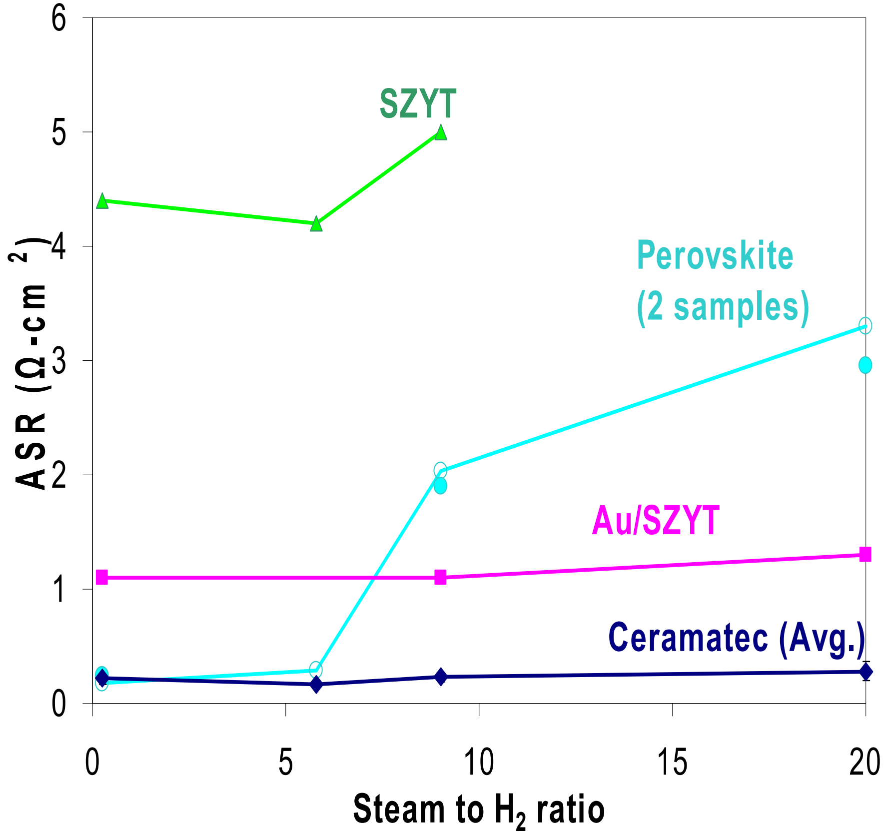




Increasing steam concentration increases ASR of steam/H_2 electrodes

- **ASR results for ZYT, LSCM, and Nb_2TiO_7 follow the same trend**
  - **ZYT = $Zr_{0.62}Y_{0.2}Ti_{0.18}O_{1.9}$**
  - **LSCM = $La_{0.25}Sr_{0.75}Cr_{0.5}Mn_{0.5}O_{3-\delta}$**
  - **SZYT = $Sc_{0.15}Zr_{0.62}Y_{0.05}Ti_{0.18}O_{1.9}$**

Temperature = 830°C



ASR = Area specific resistance

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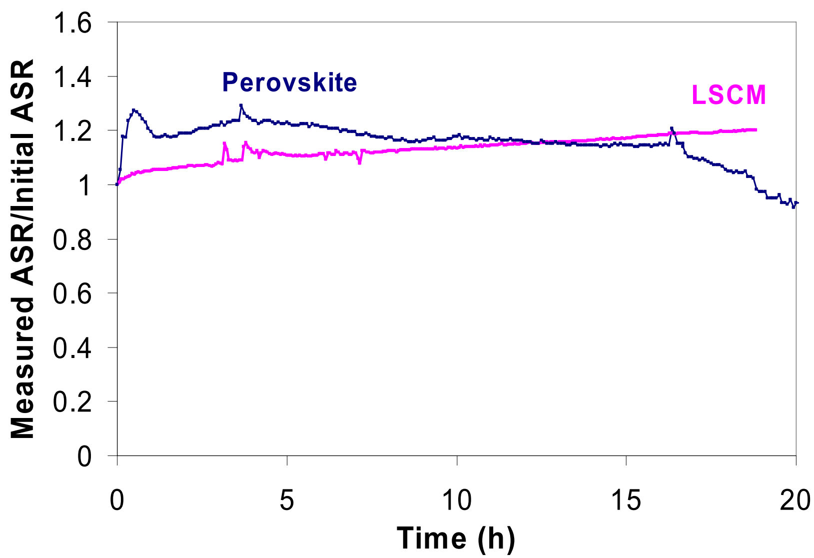
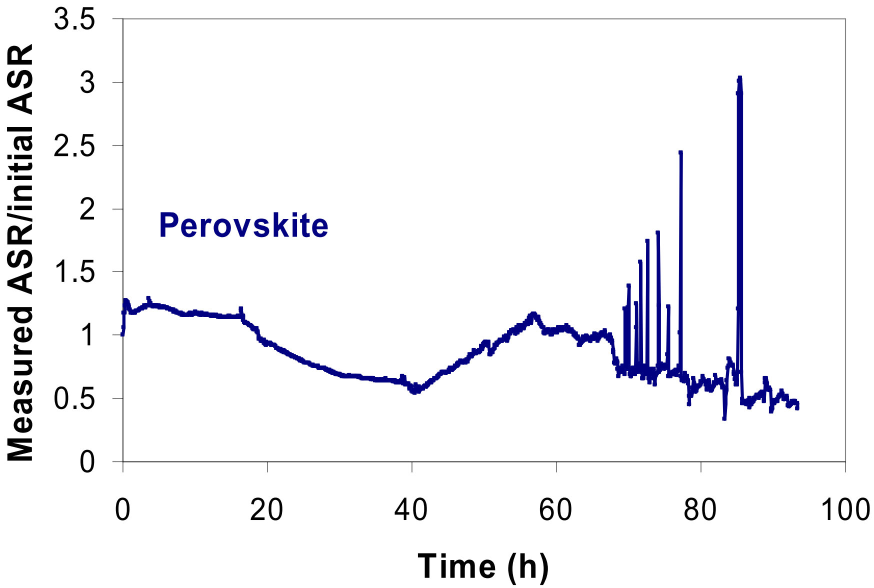
Steady state performance of steam/hydrogen electrodes shows that oxides may replace Ni-YSZ





- Temp = 830°C
- Current density = 200 mA/cm^2
- Feed gas = H_2
- Steam to H_2 ratio = 6

- Degradation of the perovskite sample is due in part to exfoliation of the counter electrode, which was made out of the same material
  - Exfoliation also occurred with Pt and Ni-CeO_2 counter electrodes

Future Work

Stack evaluation:

- Use post-test examination to evaluate Integrated Lab Scale stack
- Use XANES and XAFS to gain chemical information in areas of interest on oxygen and steam/H_2 electrodes
- Work with Ceramatec in mitigating causes of stack degradation

Oxygen and steam/H_2 electrode development:

- Prepare steam electrolysis cells and test electrode durability for 500-h operation
- Investigate Cr-poisoning
- Continue development of steam/H_2 electrode using perovskite oxides and alloys

Summary on High Temperature Electrolysis Stack Post-test Evaluation and electrode development

- **4-point resistivity measurements show**
  - **Oxygen electrodes degraded along the seal at the hydrogen exit of the stack**
  - **Steam/H_2 electrodes degraded at the hydrogen exit of the stack**
  - **The bipolar plate had a highly resistive chromium compound**
- **Raman micro-spectroscopy identified monoclinic zirconia, Cr-Al_2O_3 crystals, and Cr-spinel forming in the surface of electrodes**
- **APS X-ray fluorescence and transmission identified Cr diffusing into the electrode toward the interface and electrode thickness variations**
- **SEM analysis verified edge degradation via delamination and Sr segregation in the oxygen electrode**
- **SEM analysis of steam/H_2 electrodes identified Al and Si impurities in areas that showed high resistivity in 4-point measurements**

- **Pr_2NiO_4 with ceria interlayers show promise**
- **Perovskite compositions show potential for use as steam electrodes for HTSE**

Materials Degradation Studies for High Temperature Steam Electrolysis Systems

Paul Demkowicz, Pavel Medvedev, Kevin DeWall

Idaho National Laboratory

May 2007

Project ID #
PDP30

Overview

- **Timeline**
  - **Project start date: Jan 2006**
- **Budget**
  - **Total project funding to date**
    - $858K
  - **Funding received in FY06**
    - $492K
  - **Funding in FY07**
    - $366K

- **Barriers**
  - **Electrolysis cell/plant materials degradation**
- **Partners**
  - **Ceramatec Inc.**
  - **Argonne National Laboratory**

Objectives

- **Overall:**
  - Investigate the high temperature degradation behavior of solid oxide electrolysis cell (SOEC) and electrolysis balance-of-plant materials.
  - Identify degradation mechanisms and kinetics to help determine component lifetimes and propose new materials for long-term device operation with minimal property degradation.
- **FY07**
  - Conduct corrosion experiments on Ceramatec electrolysis cell materials

Approach

1. Develop high temperature corrosion test capability

- **Single and dual atmosphere (“bi-polar”) corrosion experiments**
- **Gas mixtures:**
  - H_2O/H_2 (*simulates cathode-side*)
  - Air/O_2 (*simulates anode-side)*
- **Temperatures to 1000ºC**
- **Safety engineering for laboratory use of H_2 and O_2**

2. Corrosion testing

- **Ceramatec SOEC materials**
  - **Ferritic stainless steel**
    - With and without proprietary rare-earth-based coatings
  - **Ni-Cr high temperature alloy**
- **Balance-of-plant materials**

3. Sample characterization

- **Corrosion kinetics**
- **Corrosion scale phase identification, thickness, and microstructures**
- **Area-specific resistivity of scale**

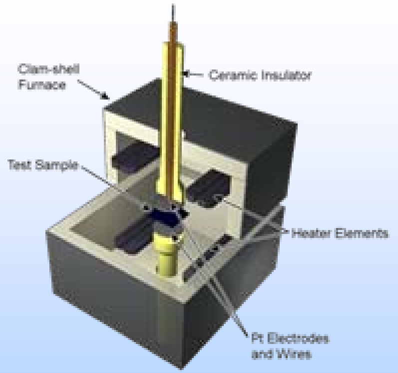
Corrosion test stand development

High temperature steam electrolysis corrosion test stand

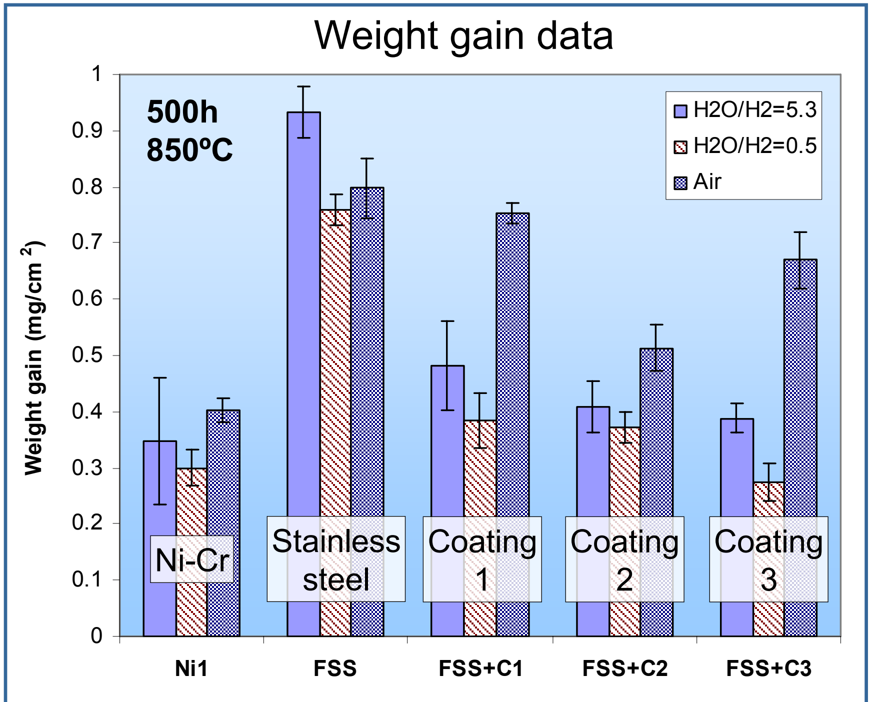
- **Three independent furnaces**
- **Three sets of parallel gas supply lines**
  1. $H_2O/H_2/N_2$ (steam provided by heated water bath)
  2. Air/O_2
- **Gas mixtures set with mass flow controllers**
- **Automatic data logging**
- **H_2 and O_2 gas safety systems:**
  - Trace He injection to detect H_2-O_2 gas cross-mixing
  - Interlocked H_2 and O_2 monitors in laboratory

Initial corrosion test results (1)

- **500 h tests completed at 850ºC with the following gas mixtures:**
  - H_2O/H_2 = 5.3, 0.5
  - Dry air
- ***Sample characterization is ongoing:***
  - ***Scale microstructures and thickness***
  - ***Scale chemistry***
  - ***Scale resistivity as a function of temperature:***

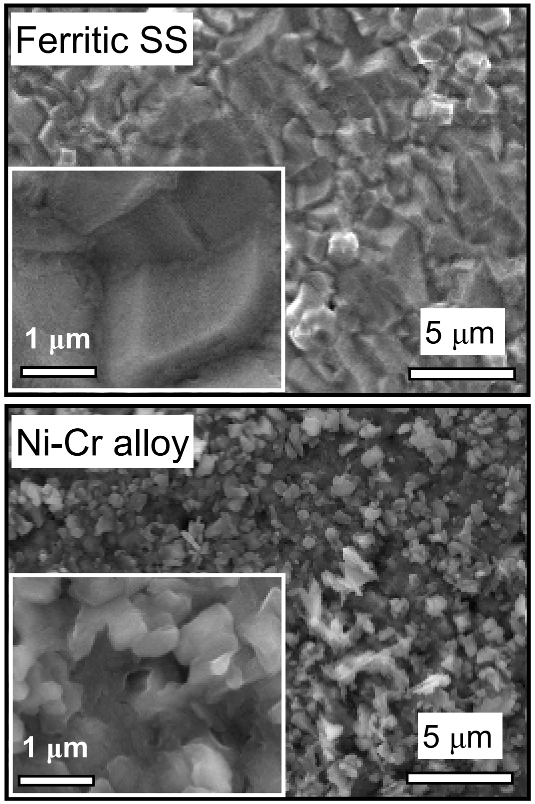


Area specific resistivity apparatus



- **Ni-Cr alloy base metal more corrosion resistant in both H_2O/H_2 and air than ferritic stainless steel**
- **Proprietary Ceramatec coatings effective in reducing corrosion in H_2O/H_2; less effective in air**

Initial corrosion test results (2)



→ $FeCr_2O_4$

→ Fe_3O_4 + Cr_2O_3

Surface microstructures of uncoated stainless steel and nickel alloy specimens and results of x-ray diffraction phase analysis
(187 h @ 825C; H_2O/H_2 = 0.9)

In H_2O/H_2:

- Ferritic stainless steel forms chromite ($FeCr_2O_4$)
- Ni-Cr alloy forms duplex layer of magnetite (Fe_3O_4) and chromia (Cr_2O_3)

Future work

FY07

- **Complete initial corrosion tests (Apr 2007 milestone) and sample characterization**
- **Select candidate electrolysis balance-of-plant materials for future tests**

FY08

- **Perform long term (> 1000 h) corrosion tests on electrolysis cell and balance-of-plant materials**
- **Construct dual atmosphere corrosion cell and perform corrosion tests on metallic interconnects**

Summary

Relevance:	Address issues with materials degradation in SOECs and in balance-of-plant components that can affect process efficiency and operational lifetimes.
Approach:	Conduct corrosion tests on electrolysis cell and plant component materials to assess material performance and degradation behavior.
Accomplishments:	Built corrosion test stand; performed initial 500 hour tests on Ceramatec electrolysis cell materials (in progress); demonstrated coating effectiveness in corrosion inhibition
Future work:	Perform long term tests on electrolysis cell and balance-of-plant materials; construct experimental apparatus and perform dual-atmosphere corrosion studies on metallic interconnect materials.

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SO_3 Electrolysis: Reduced Temperature Sulfur-Iodine Cycle

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SO_3 Electrolysis: Reduced Temperature Sulfur-Iodine Cycle

Sulfur-Iodine cycle to produce hydrogen:

$2H_2O_{(l)} + SO_{2\,(g)} + I_{2\,(l)} \rightarrow H_2SO_{4\,(l)} + 2\,HI_{(l)}$ 120°C

$H_2SO_{4\,(l)} \rightarrow H_2O_{(g)} + SO_{3\,(g)}$ ~500°C

$SO_{3\,(g)} \rightarrow SO_{2\,(g)} + \frac{1}{2}O_2$ ~850°C

$2HI_{(g)} \rightarrow I_{2\,(l)} + H_2$ ~400°C

High Temperature

Reduce temperature by electrochemical reduction (electrolysis)

$SO_3 \rightarrow SO_2 + \frac{1}{2}\,O_2$ + electricity 500-600ºC E°=0.11 V

Overview

Timeline

- Start – Oct 2005

Budget

- FY06 - $164k
- FY07 -$120k

Barriers

- Economical production of hydrogen from water
- High temperature of sulfur-iodine thermochemical cycle
- Electrode stability and activity in corrosive H_2O-SO_2-SO_3 atmosphere

Objectives

- Determine feasibility of SO_3 electrolysis to reduce temperature of Sulfur-Iodine thermochemical cycle to 500-600°C
- Build electrochemical test reactor to develop and test SO_3 electrodes
- Develop electrochemical cell materials to build SO_3 electrolyzer
  - Oxygen electrodes
  - SO_3 electrodes

Approach

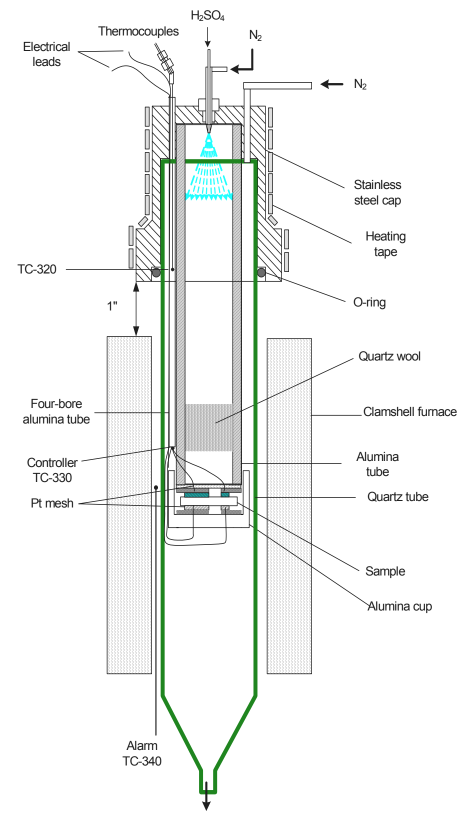
- **Build single atmosphere $H_2O/SO_2/SO_3$ test reactor to analyze candidate SO_3 electrodes**

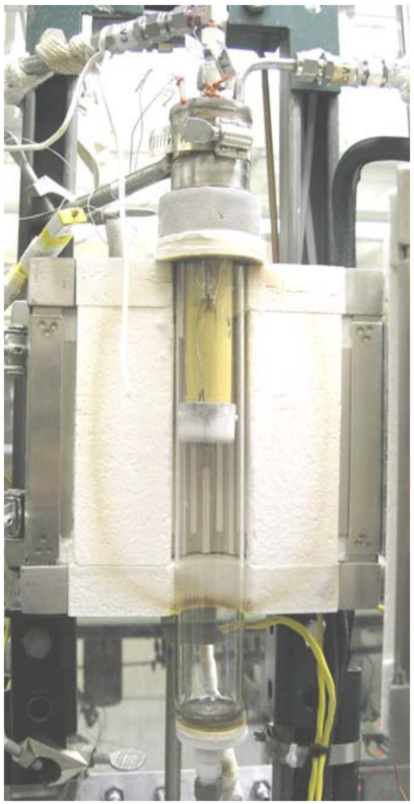
- **Determine elements that are thermodynamically stable in SO_2/SO_3 atmosphere**

- **Fabricate new SO_3 electrodes based on thermodynamic study and understanding of ceramic electrochemical devices**

SO_3 electrode test fixture

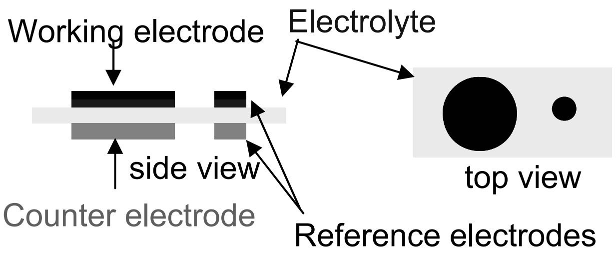
- H_2SO_4/H_2O mixture is sprayed into sample tube above the cell
- O_2 and SO_2 monitored by mass spectrometry





Results:

- Electrochemical cell was shown by cyclic voltammetry to reduce some SO_3 to SO_2



Stability diagrams help identify candidate electrode elements

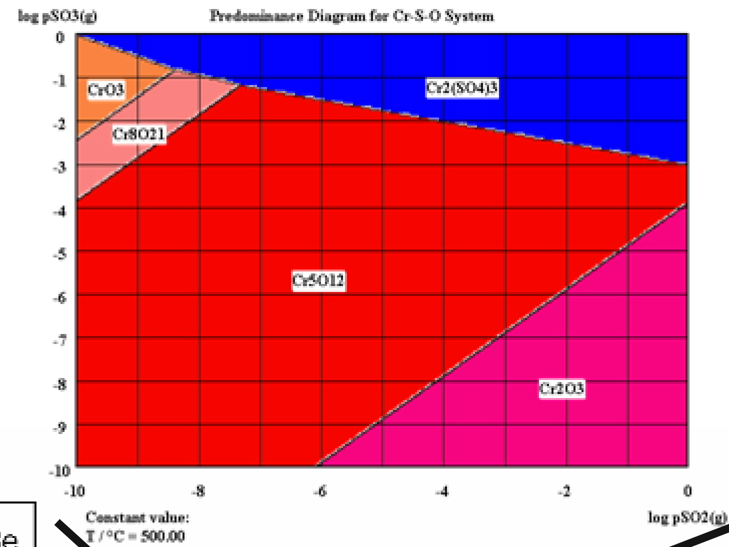
- Calculated predominance diagrams illustrate stable phases in SO_2-SO_3
  - Blue = Sulfate *undesirable*
  - Red = Oxide
  - Yellow = Metal

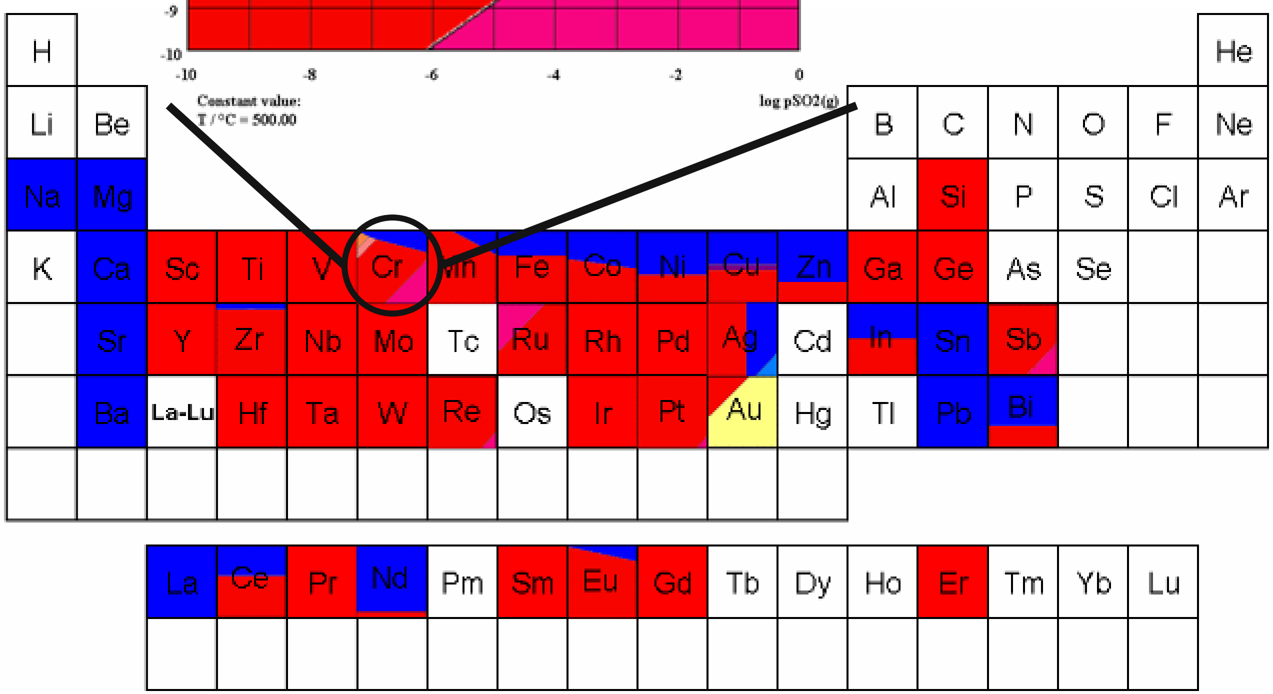
- Gold is only stable metal

- Traditional SOFC electrodes are not stable in SO_2/SO_3

- Candidate oxide has been identified, fabricated and tested as electrodes, others being fabricated

Example:
Chromium Predominance Diagram





Future Work

- Fabricate, test and improve SO_3 electrodes
- Develop cell design for the SO_3 electrolyzer

Summary

- Electrochemical test stand built to test SO_3 electrodes
- Cell containing Pt electrodes showed electrolysis by cyclic voltammetry
- Periodic element chart was developed to identify possible candidates for SO_3 electrode materials