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Materials Issues and Experiments for HTE and SO_3 Electrolysis

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Project #PDP30

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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**

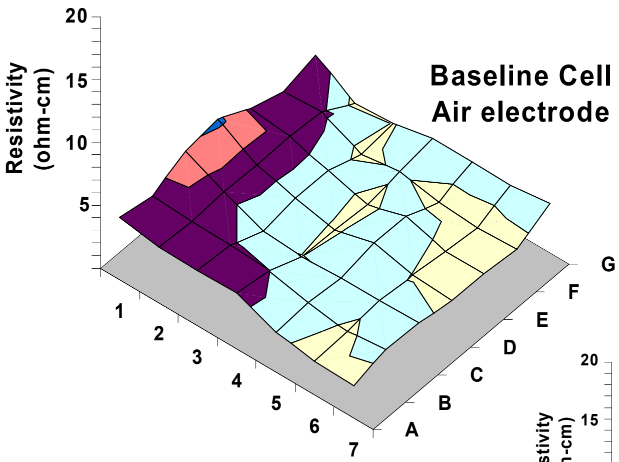
2) **Improved oxygen and steam/hydrogen electrodes**
   - **Pr_2NiO_4 - polarization, stability tests**
   - **$La_{1-x}Sr_xMn_{1-x}B_xO_3$ B= Cr, Al, Ga – polarization, stability tests**

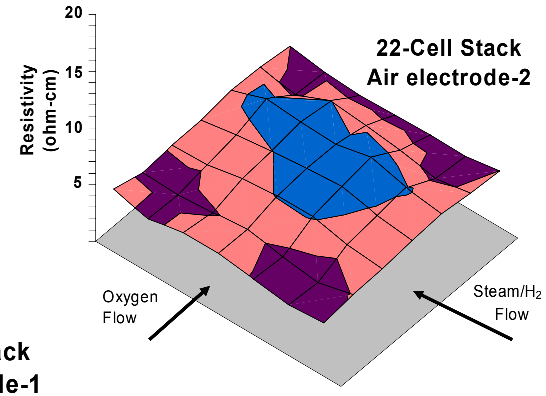
Resistivity maps for oxygen electrodes show degradation at hydrogen exit of cell

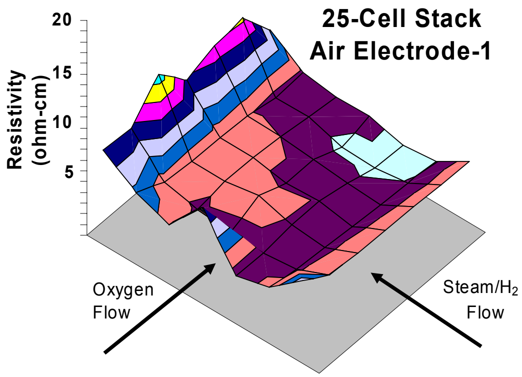
- Baseline Cell (untested) reasonably flat resistivity. 2-6 ohm-cm

- 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

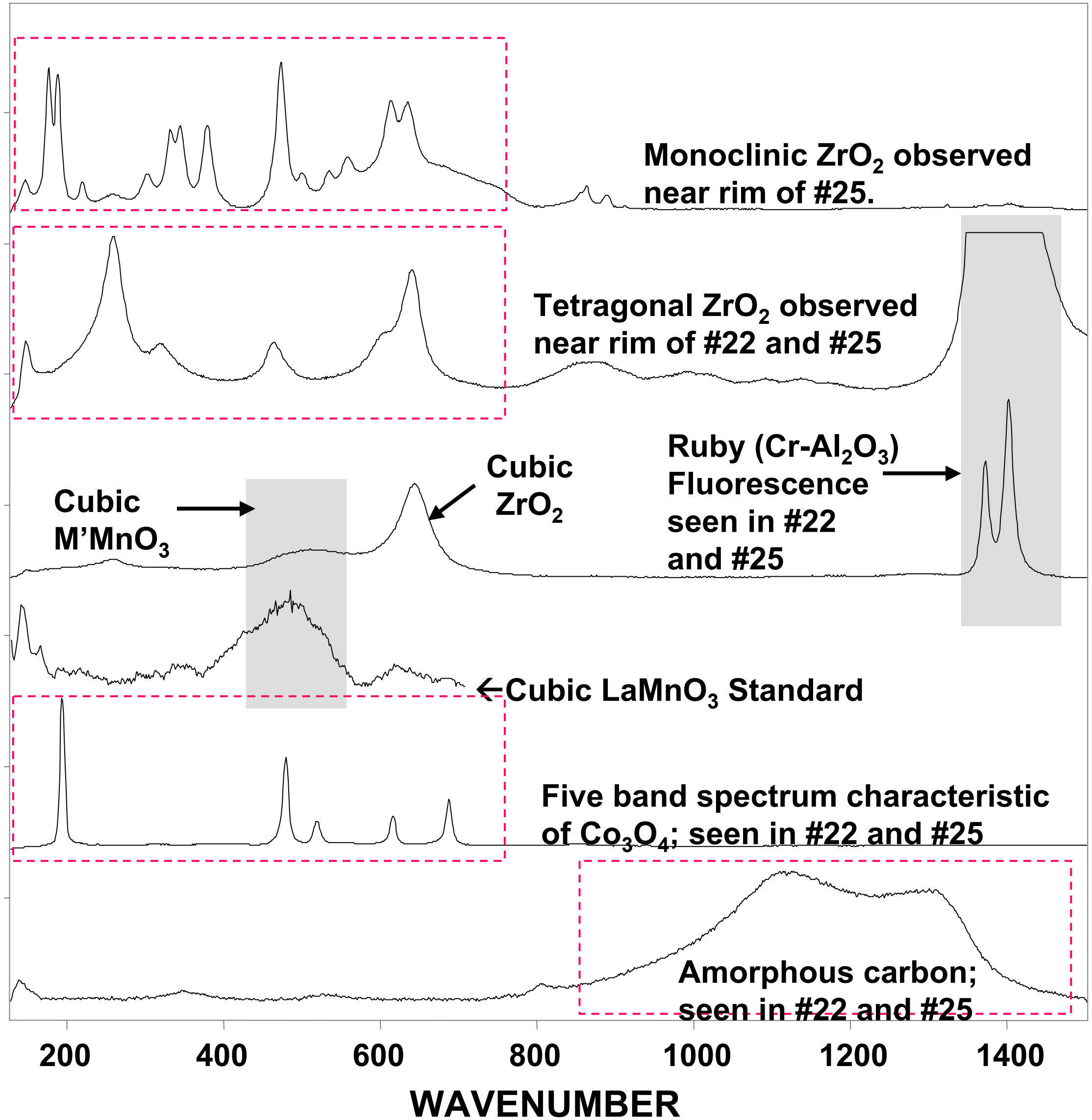






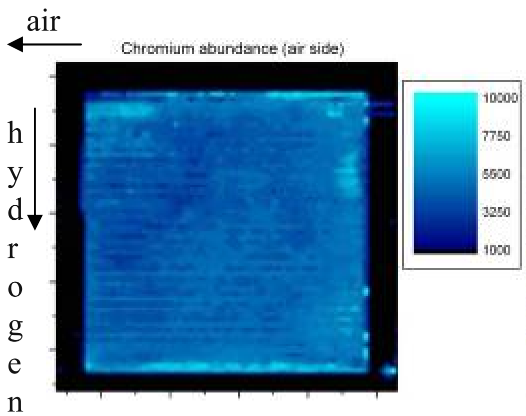
Raman micro-spectroscopy on oxygen electrodes identifies unexpected phases

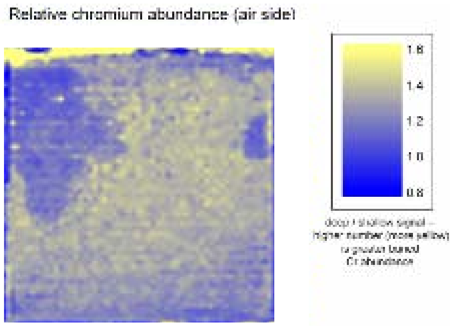
- **Monoclinic zirconia observed on exposed edges of the ScSZ plate**
- **Chromium reacted with Al in sealant near edge of electrode**

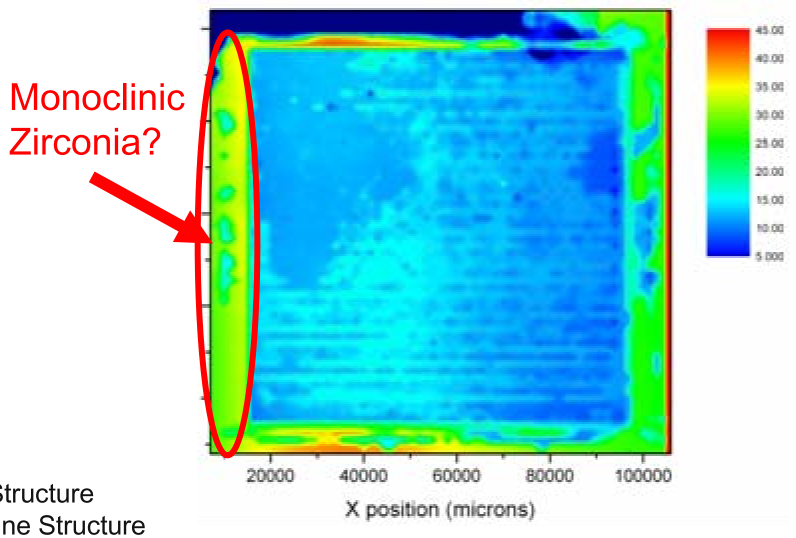


X-ray fluorescence and transmission show Cr migration and thickness variations in the cell

- 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

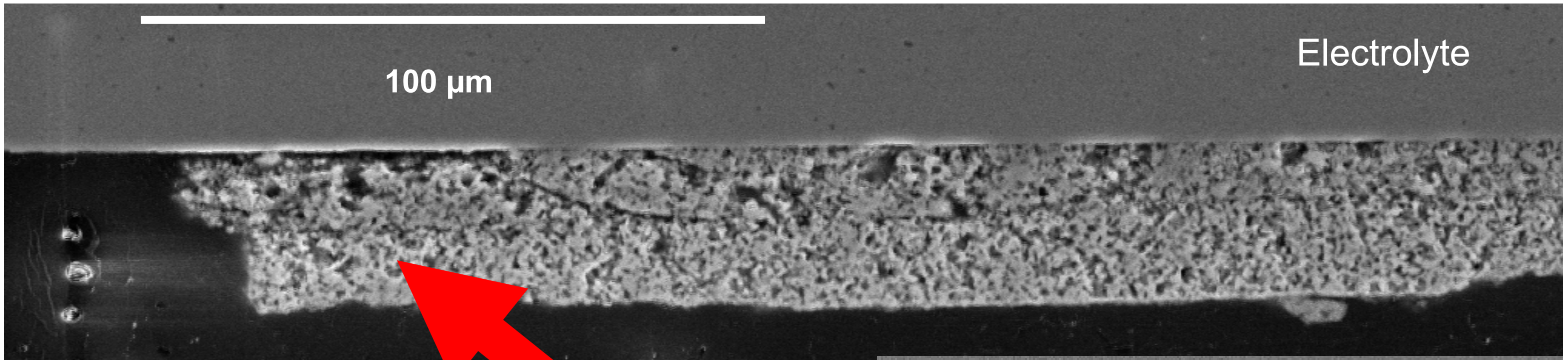


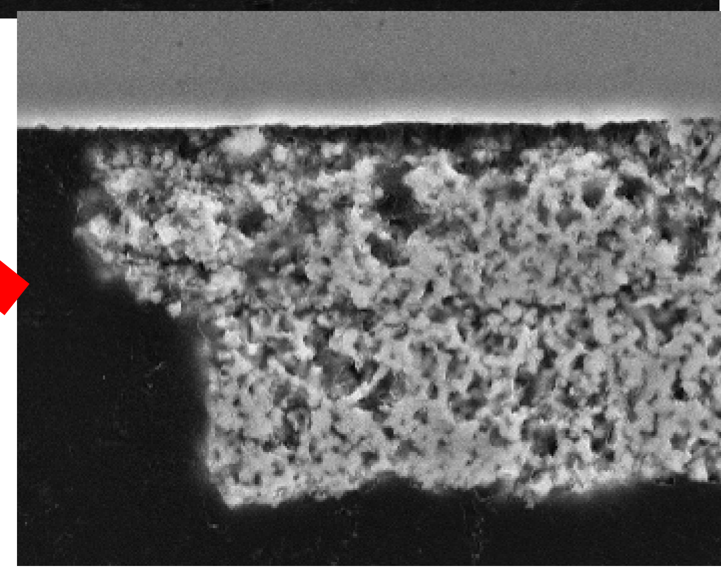




XANES: X-ray Absorption Near Edge Structure
EXAFS: Extended X-Ray Absorption Fine Structure

SEM analysis of oxygen electrode shows delamination in the oxygen electrode

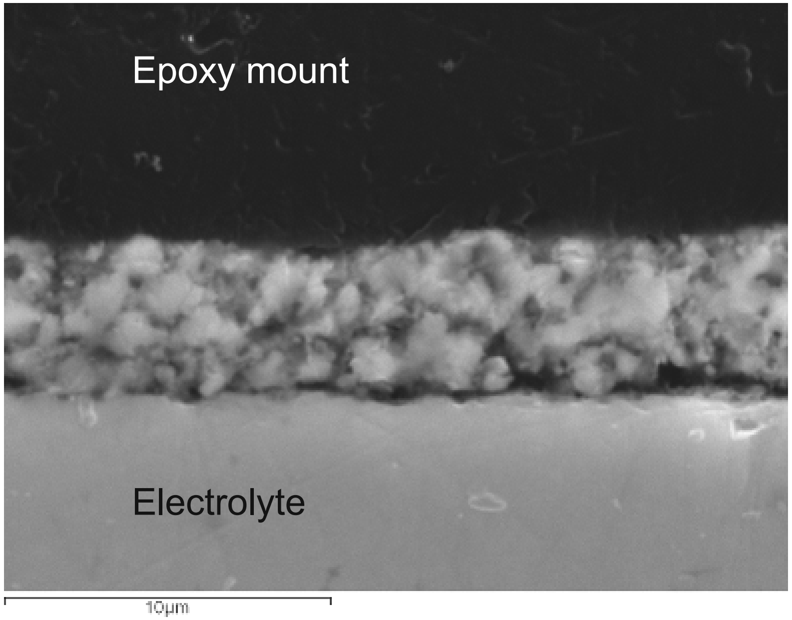




- **Delamination near the edge of the oxygen electrode was found where high resistance was measured with the 4-point probe**
- **Internal defaults were also seen near the edge**

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

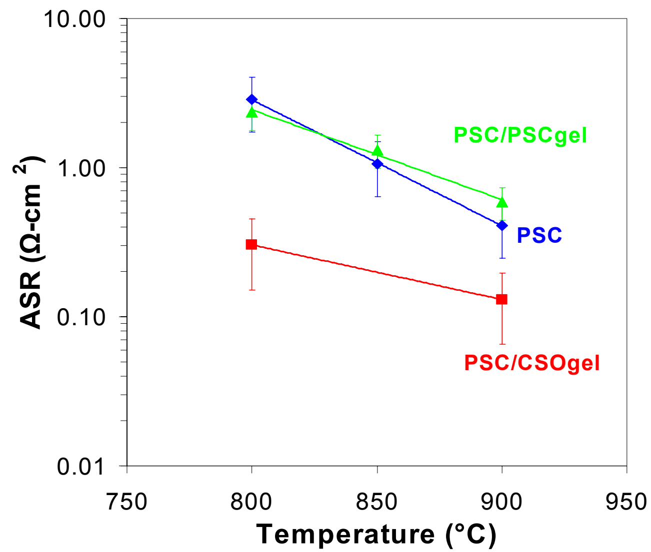
- **Area with low resistivity on 4-point probe maps:**
  - **Al present at electrode/bond layer interface**
  - **More Al near the sealed edge (Al:Ce = 0.05 – 0.25)**
- **Area with high resistivity on 4-point probe maps (at the edge):**
  - **More Si found near where bond layer was removed (Si:Ce = 0.05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

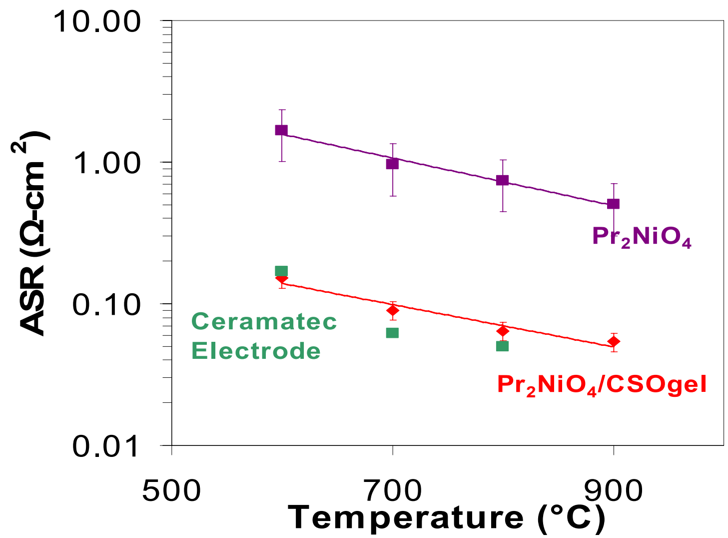


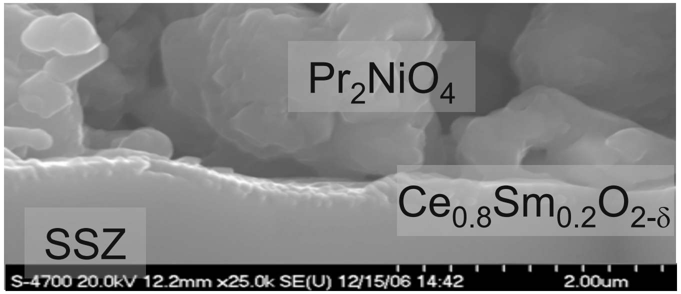
- **Increased contaminants near the sealed edges indicate that the seal material may be the source of Si and Al**

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

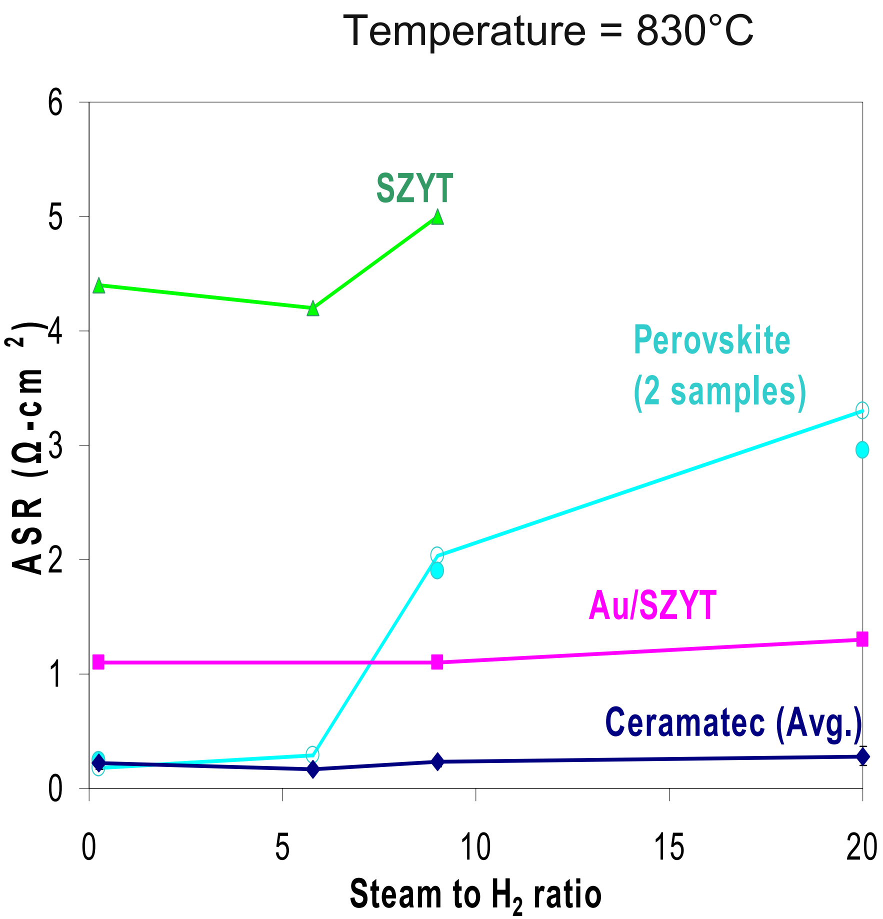






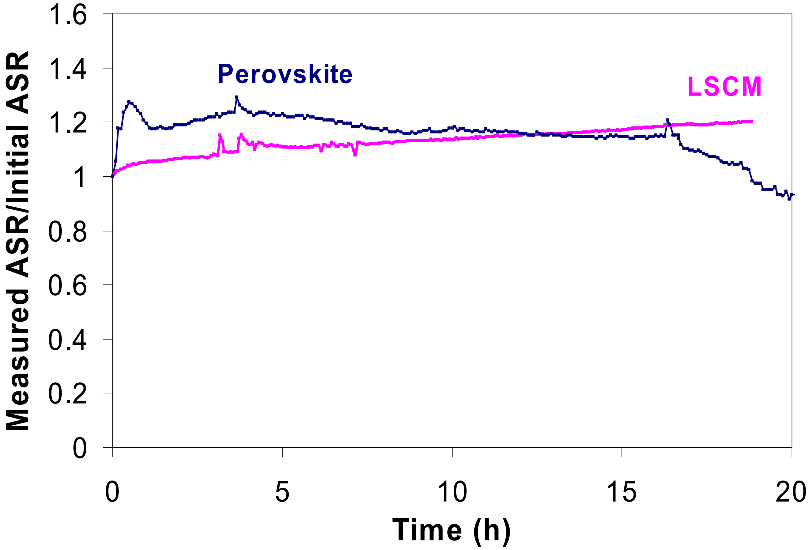
Increasing steam concentration increases ASR of steam/H_2 electrodes

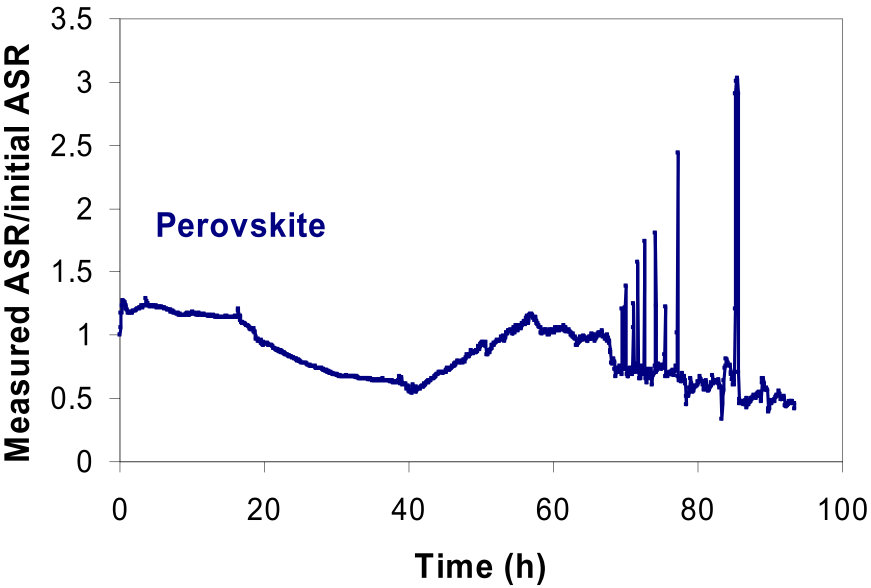
- **ASR results for ZYT, LSCM, and Nb_2TiO_7 follow the same trend**
  - **ZYT = $Zr_{0.62}Y_{0.2}Ti_{0.18}O_{1.9}$**
  - **LSCM = $La_{0.25}Sr_{0.75}Cr_{0.5}Mn_{0.5}O_{3-\delta}$**
  - **SZYT = $Sc_{0.15}Zr_{0.62}Y_{0.05}Ti_{0.18}O_{1.9}$**



ASR = Area specific resistance

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**

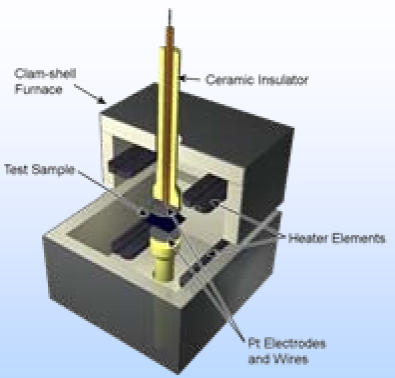
Corrosion test stand development

High temperature steam electrolysis corrosion test stand

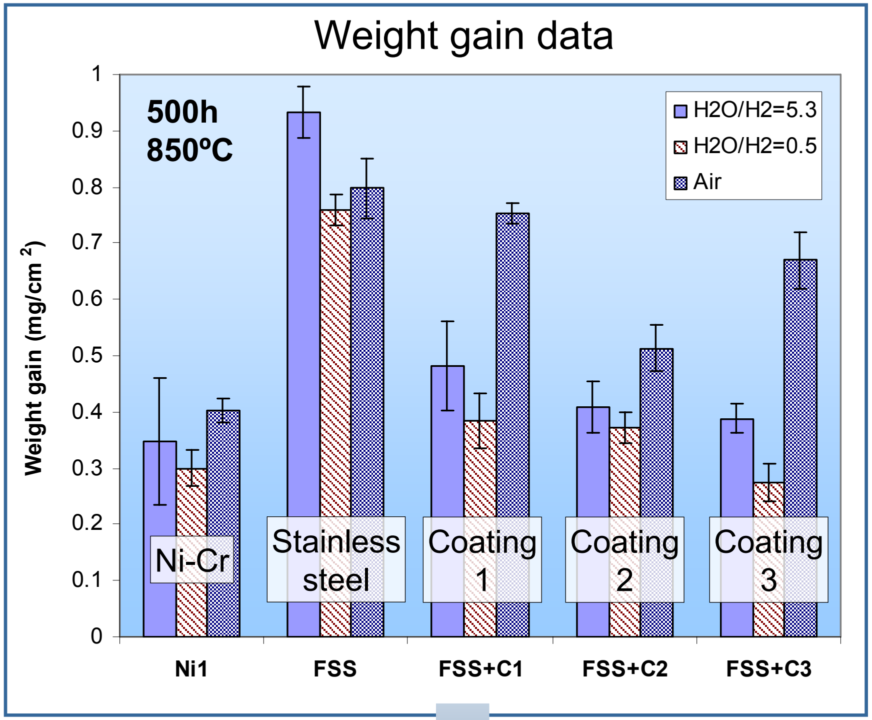
- **Three independent furnaces**
- **Three sets of parallel gas supply lines**
    1. $H_2O/H_2/N_2$ (steam provided by heated water bath)
    2. Air/O_2
- **Gas mixtures set with mass flow controllers**
- **Automatic data logging**
- **H_2 and O_2 gas safety systems:**
    - Trace He injection to detect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

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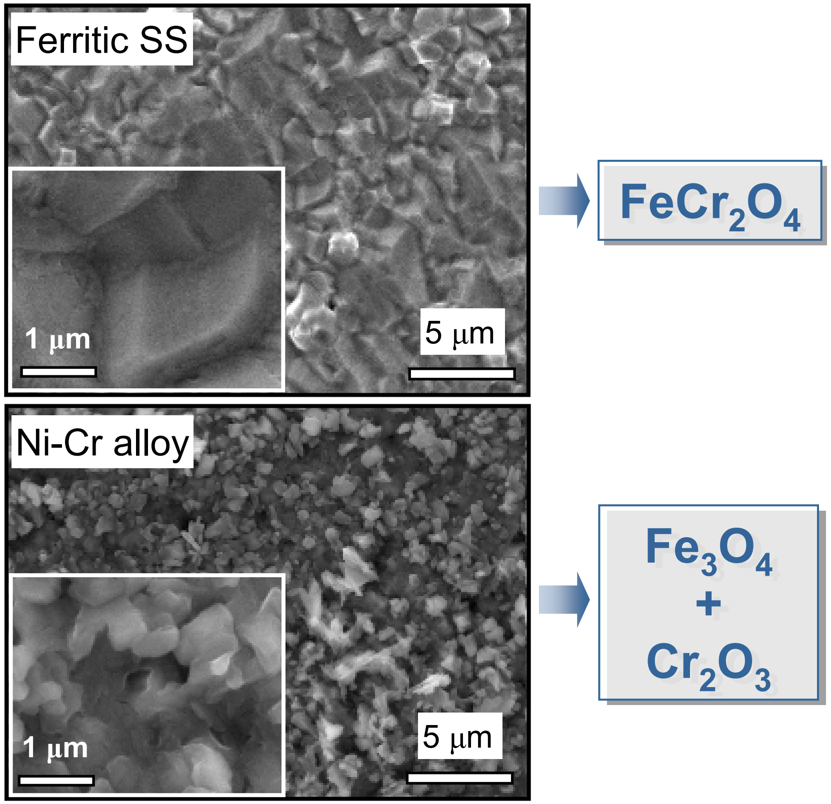
Initial corrosion test results (2)



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
$SO_{3\,(g)} \rightarrow SO_{2\,(g)} + ½O_2$	~850°C
$2HI_{(g)} \rightarrow I_{2\,(l)} + H_2$	~400°C

High Temperature

Reduce temperature by electrochemical reduction (electrolysis)

$SO_3 \rightarrow SO_2 + ½\,O_2$ + 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**

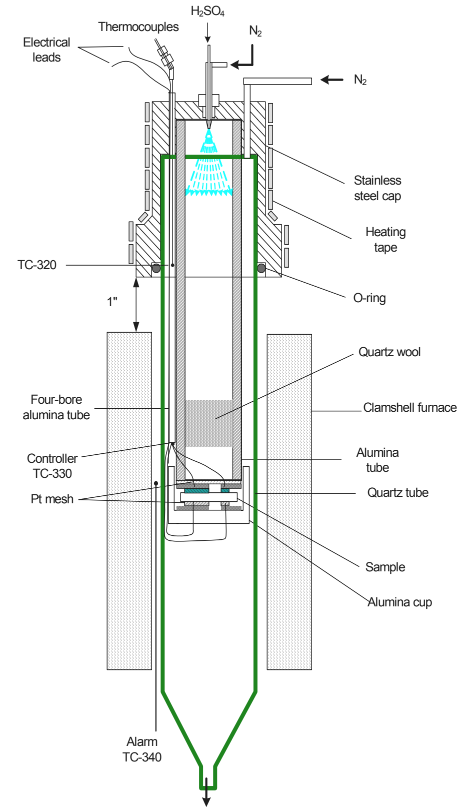
- **Develop electrochemical cell materials to build SO_3 electrolyzer**
  - **Oxygen electrodes**
  - **SO_3 electrodes**

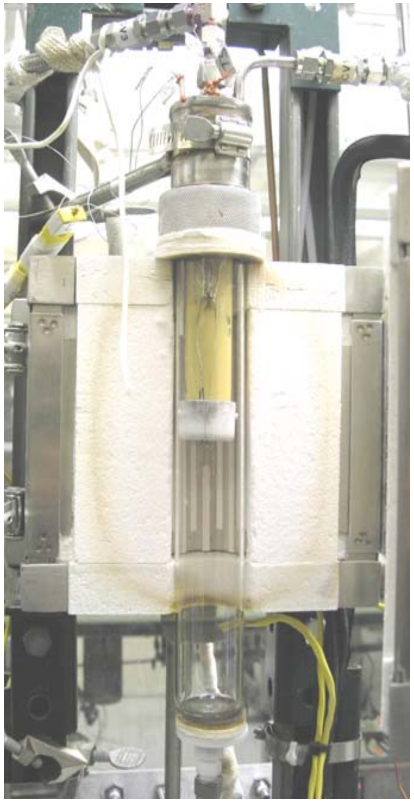
Approach

- **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

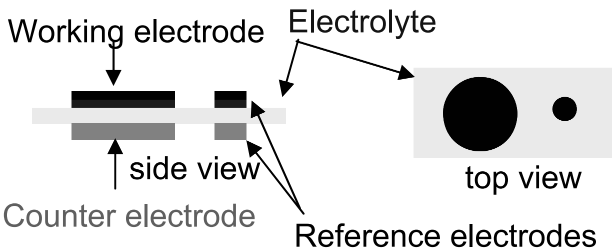
- H_2SO_4/H_2O mixture is sprayed into sample tube above the cell
- O_2 and SO_2 monitored by mass spectrometry





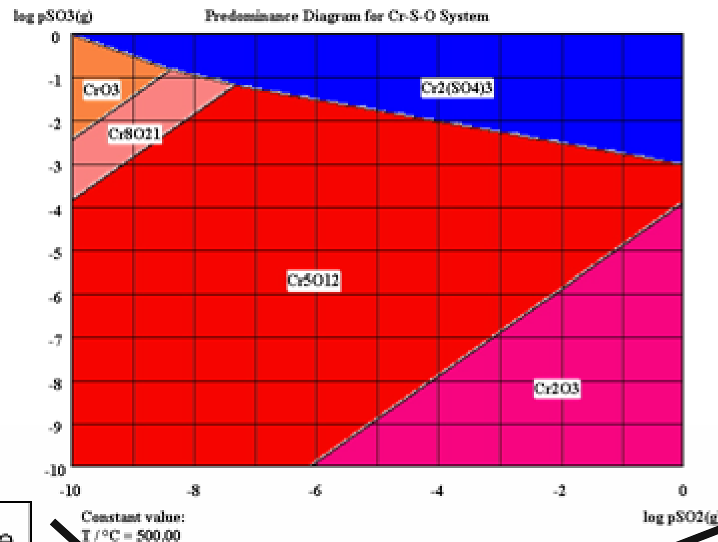
Results:

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



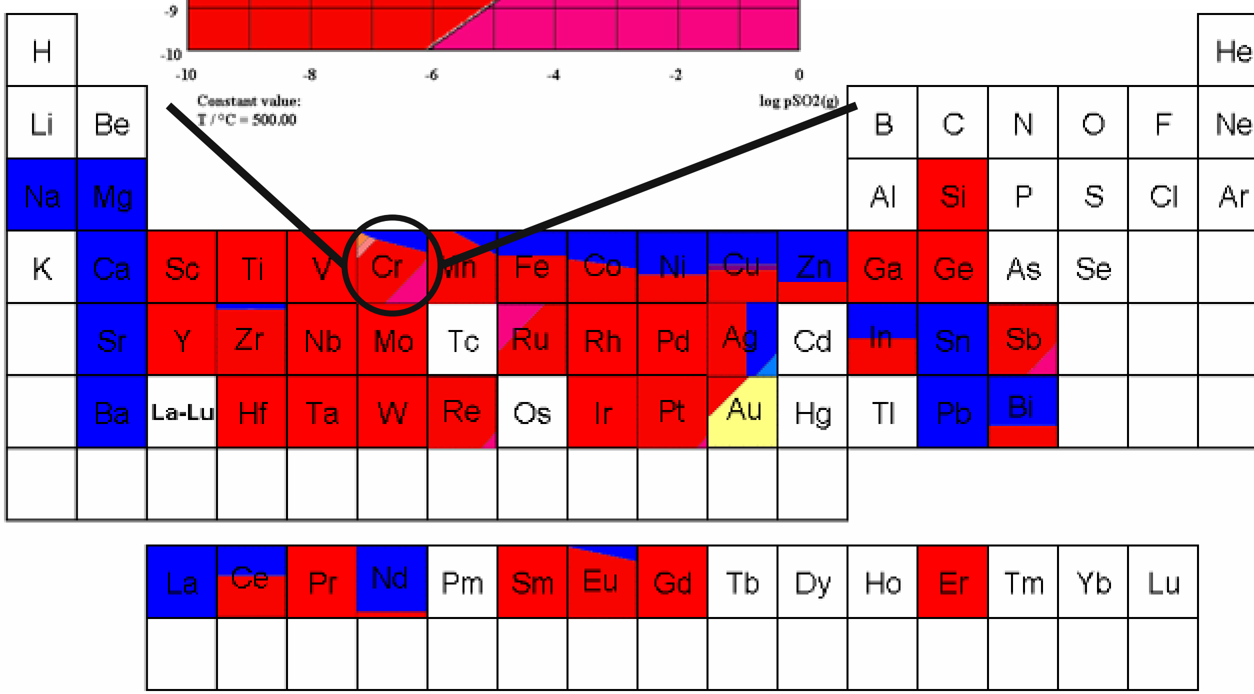
Stability diagrams help identify candidate electrode elements

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



Example:
Chromium Predominance Diagram

- 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



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