Electrodes for PEMFC Operation on H_2 and Reformate

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Hydrogen, Fuel Cells and Infrastructure Technologies Program
Annual Review, Berkeley, CA, May 2003

Los Alamos
NATIONAL LABORATORY

Response to Comments from 2002 Review

* Investigate long term stability of the Adzic catalyst.

  → *A 500 hr FC test with this catalyst (1 wt%Pt-10 wt%Ru) is currently in progress. New improved catalyst will be tested.*

* Should focus on development of evaluation "tools" to identify better electrodes.

  → *In addition to traditional electrochemical methods, fundamental relationships between electrode structure and properties were studied with newly developed methods such as scanning XRF imaging, simultaneous measurement of catalyst layer electronic and ionic conductivities and catalyst layer porosity measurements.*

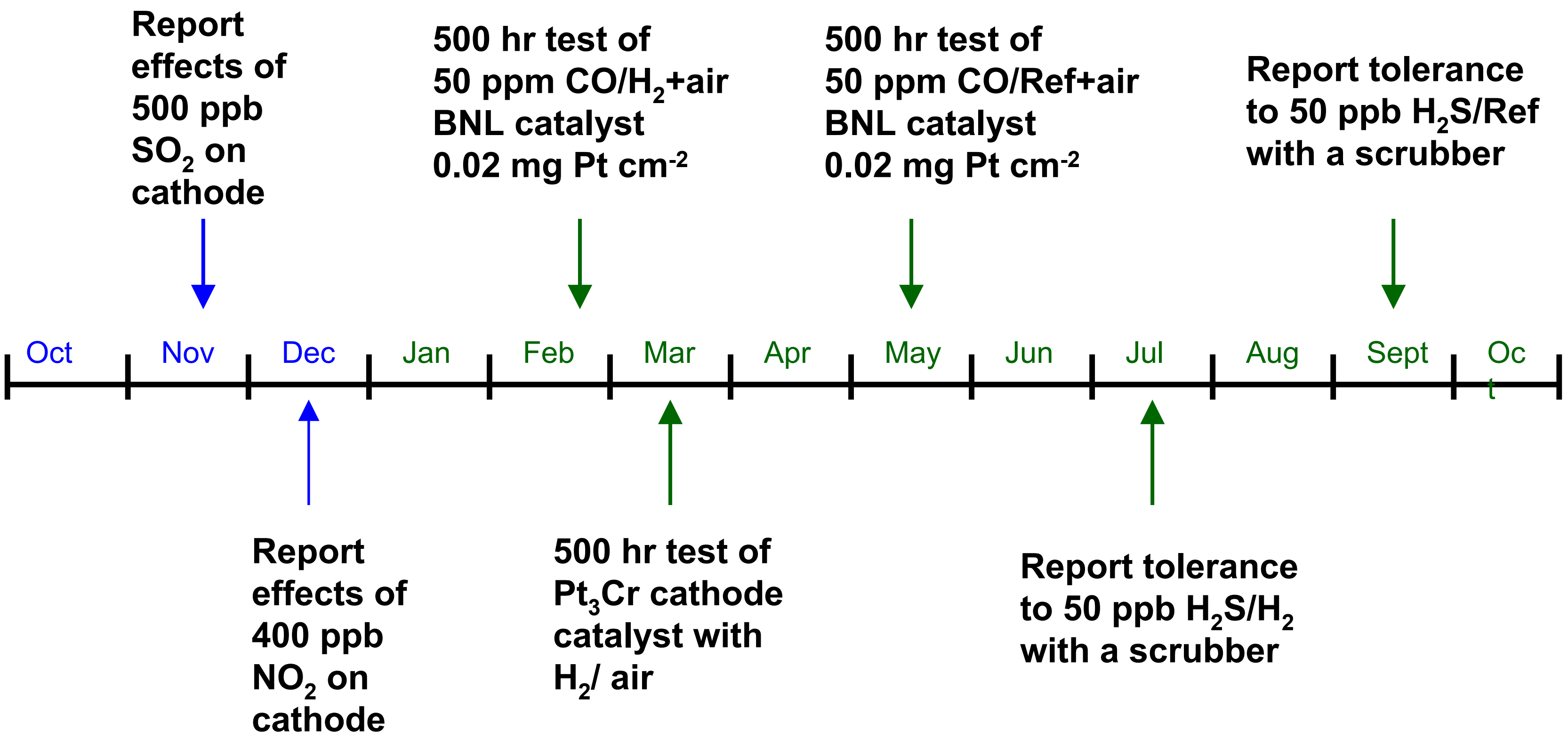
* Emphasize interactions that develop more fundamental understanding of catalyst and electrodes.

  → *On going collaborations with ORNL and BNL for studying MEA structure and low Pt content catalysts.*

* Appropriate project for national laboratory to develop tools and criteria to evaluate catalyst and electrode performance from a neutral perspective.

  → *LANL is a key participant in developing and performing the "single cell test protocol", implemented by the U.S.Fuel Cell Council in collaboration with private industry.*

Work Timeline



Collaborations and Outreach Activities

Donaldson (E. Stenersen) **: Ambient air impurities** (CRADA)

DuPont: MEA evaluation (CRADA)

SMP (P. Atanasova)**: Catalyst Testing**

OMG: Catalyst Testing

TKK: Catalyst Testing

Brookhaven NL (R. Adzic)**: Evaluation of low Pt content catalysts**

Navy Research Laboratory: LANL hosted researchers

USA Fuel Cell Council: Single cell test protocol

Presentations at: ACS Asilomar Meeting, ECS Mtg., FC Seminar, FreedomCar Technical Team Mtg., Alabama EPSCOR workshop.

Anode Work: Goals and Approach

Overall Goal: Improve CO Tolerance and study the effects of other impurities on FC performance

* Improve tolerance to CO using reconfigured anodes (RCA) while optimizing air bleed

* Develop and test new materials for reconfigured anodes

* GC measurements for understanding RCA operation

* Evaluate low Pt content catalysts (R. Adzic, BNL)

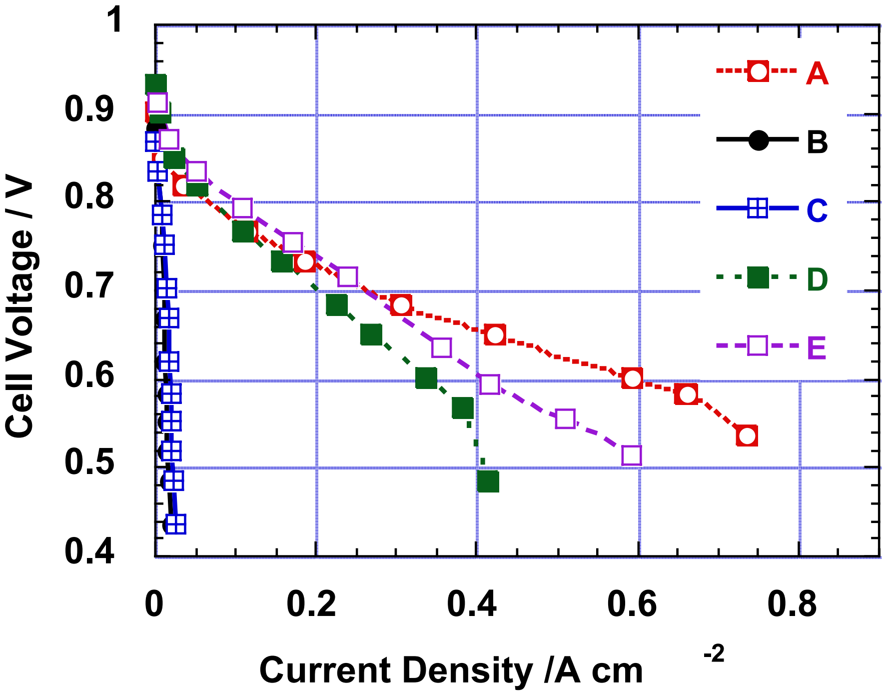
* Study effects of impurities on electronic and ionic conductivity of the catalyst layer

* Model various " poisoning mechanisms"

* Diagnostic Tools:
  - Advanced Segmented Cell
  - Method for measuring ionic and electronic conductivities in the catalyst layer

Incomplete Tolerance to 500 ppm CO in Synthetic Reformate

Reconfigured Anode = Fe_3O_4 + Fe_2O_3 on C



A RCA, Pt (0.2 mg cm^{-2}), No CO and No Air
B RCA, Pt (0.2 mg cm^{-2}), 500 ppm CO, No air
C RCA, Pt (0.2 mg cm^{-2}), 500 ppm CO + 6% air
D No RCA, Pt-Ru (0.1 mg Pt cm^{-2}), 500 ppm CO + 6% air
E RCA, Pt-Ru (0.1 mg Pt cm^{-2}), 500 ppm CO + 6% air

Even 6% air-bleed makes practically no difference with a Pt anode.

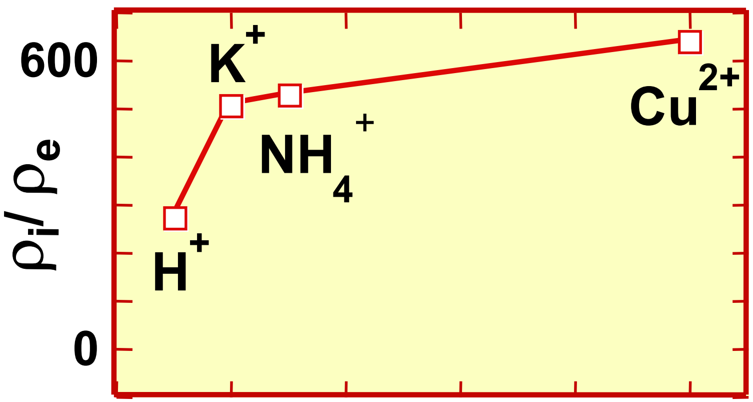
The RCA layer improves CO tolerance of Pt-Ru anode in the presence of 6% air. However, above about 0.35 A cm^{-2}, tolerance is incomplete.

Full tolerance in synthetic reformate has been demonstrated for up to 250 ppm CO.

Effect of contaminant ions on catalyst layer ionic resistivity

Nafion Form	$\frac{\rho_{ionic}}{\rho_{electronic}}$
H^+	273
K^+	504
NH_4^+	528
Cu^{2+}	640

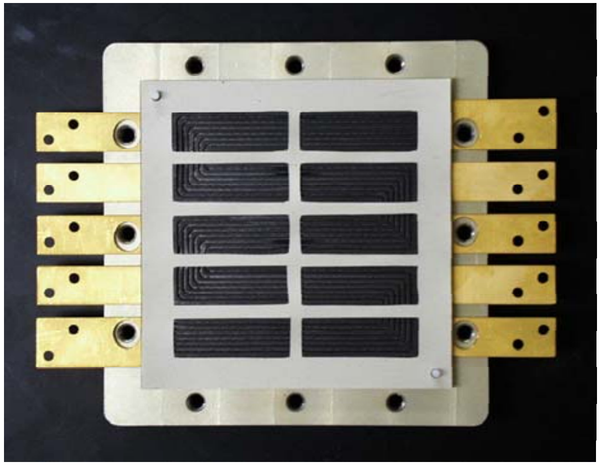
$\rho_{electronic} \approx 1\ \Omega \cdot cm$ all cases



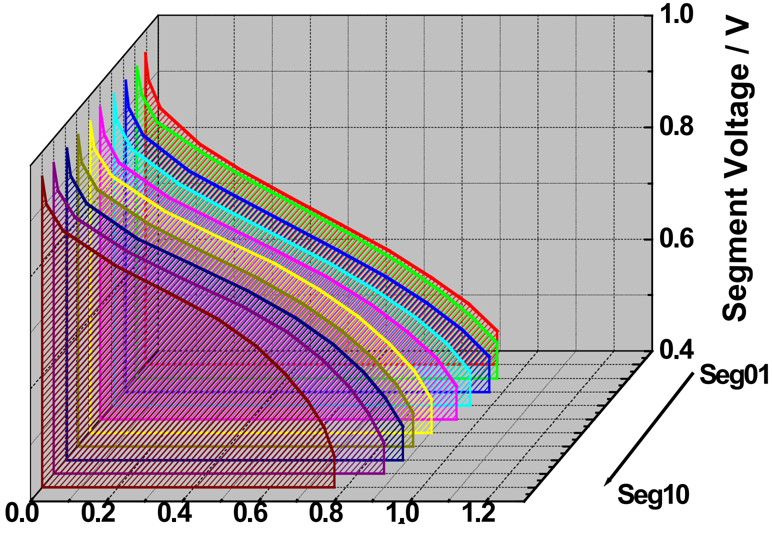
Relative Ion Exchange Selectivity for Sulfonated Polystyrene (Arb. Units)

- When H^+ in catalyst layers containing acid-form Nafion is exchanged for other ions, an increase in ionic resistivity results
- The increase in resistivity parallels the trend in ion exchange selectivity of sulfonate ionomer

Advanced Segmented Cell Hardware and Test



Segment area: 7.71 cm^2



New characteristics of cell hardware:

* Faster time resolution (10 samples/sec)
* AC Impedance measurements possible
* Highly reproducible segmented MEA electrodes

Objectives:

* measure current, voltage, HFR distribution
* study spatial CO and CO coverage
* optimize flow-field design and water management

Observations

* current distribution not homogeneous
* downstream effects along the flow channel
* water management issues
* performance enhancement possible

Anode: 810 sccm H_2, T_A=105°C, p=30psig

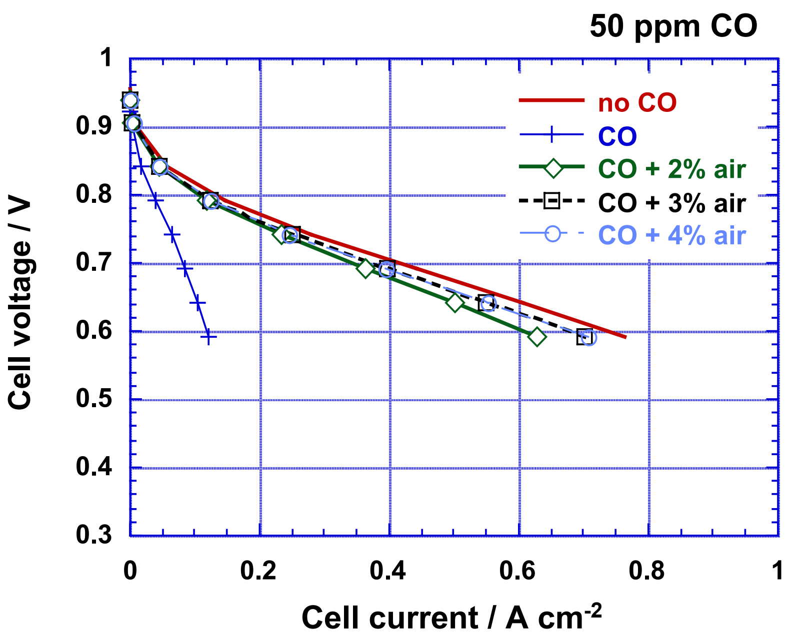
Cathode: 4000 sccm Air, T_C=80°C, p=30psig

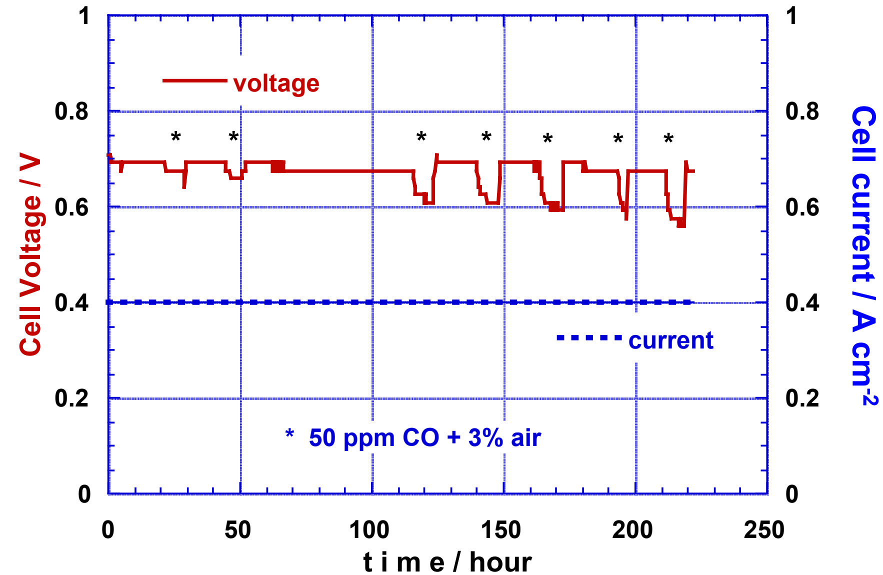
Cell temp. = 80°C, 0.2 mg Pt/cm^2 at each electrode

Low Pt Content Catalyst Long Term Test

Carbon supported 1 wt% Pt - 10 wt%Ru catalyst (R. Adzic, BNL)

Anode Pt Loading: 19 μg/cm^{-2}





50 cm^2 H_2/Air cell at 80 ^oC
A: 0.21 mg total metal/cm^2
C: 0.20 mg Pt/ cm^2
1.5 H_2 stoich

- **48.5 hrs operation with 50 ppm CO + 3% air**
- **Performance loss of 100 mV after 222 hr of operation at 0.4 A/cm^2**

Cathode Work: Goals and Approach

Goals : Improve cathode performance at high voltages
New catalyst development
Investigate effects of air impurities

* Work with catalyst suppliers to develop improved cathode catalysts

* Evaluate catalysts with high Pt content but small particle size

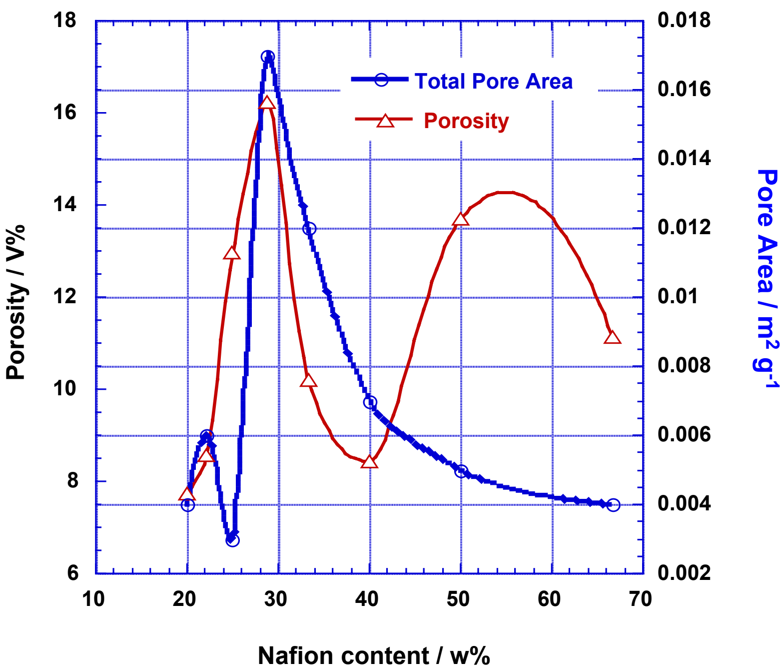
* Study cathode structure and performance relationship: New diagnostic tools (Porosimetry studies, XRF imaging)

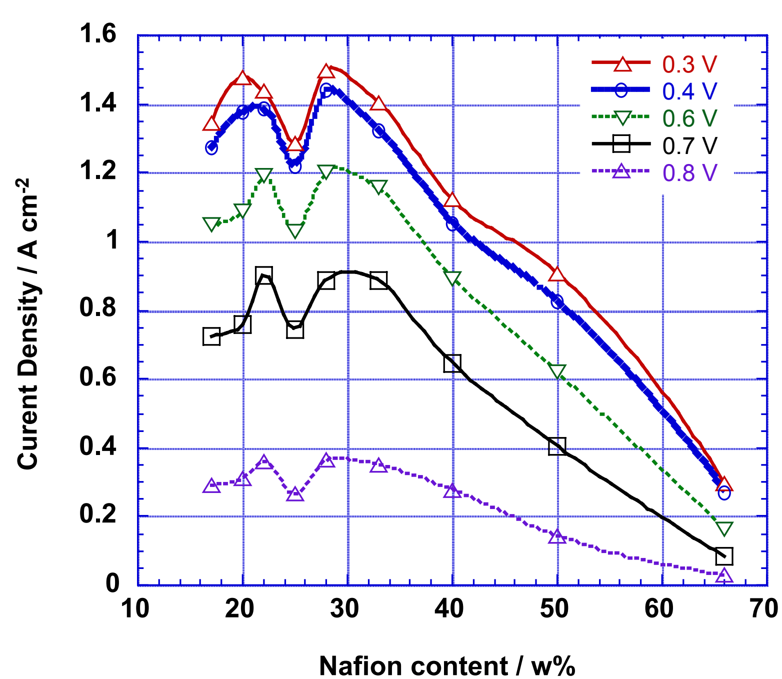
* Evaluate long term performance of Pt-Alloys

* Plan for non-precious metals catalysts development

* Study the effect of ambient air impurities on cathode performance (SO_2, NO_2, sea water, diesel soot, hydrocarbons)

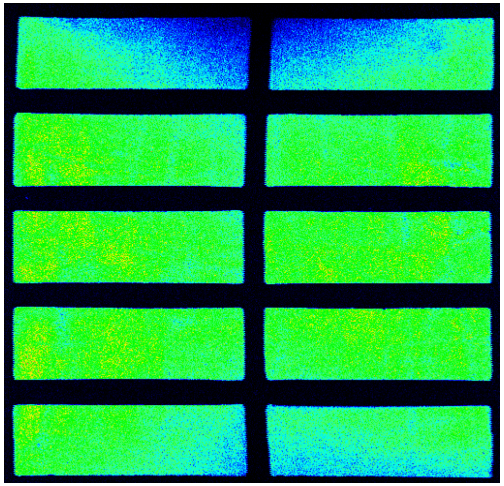
Pt_3Cr Catalyst Layer Porosimetry Data and Cathode Performance as a Function of Nafion Content



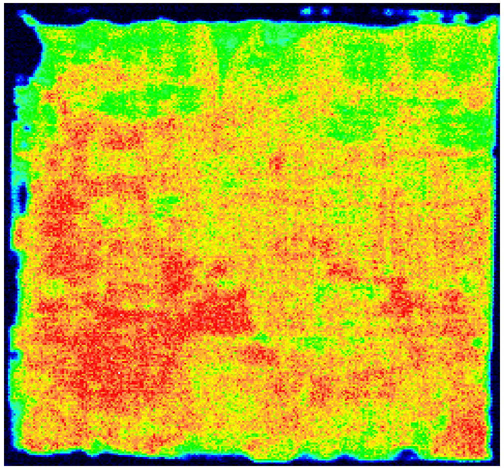


- **Porosimetry data demonstrates good correlation between MEA Nafion content and current density**

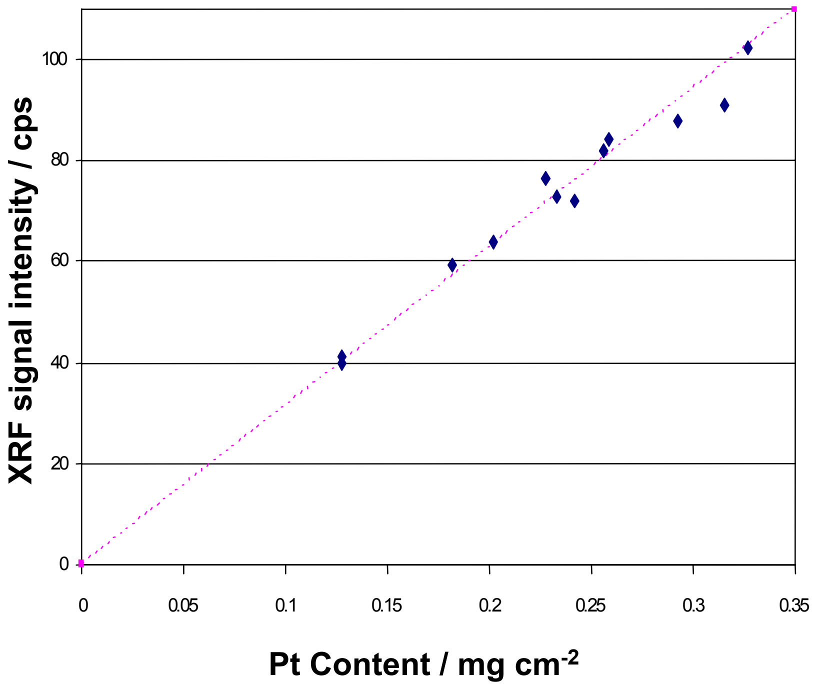
XRF Imaging and Pt Content



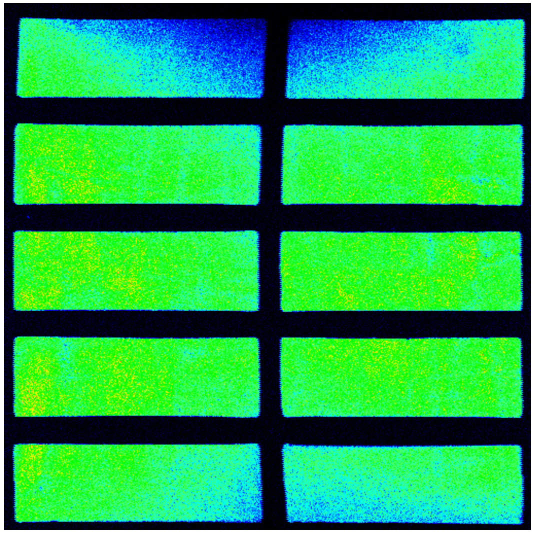
Anode side
Pt M-Line
(doctor bladed)

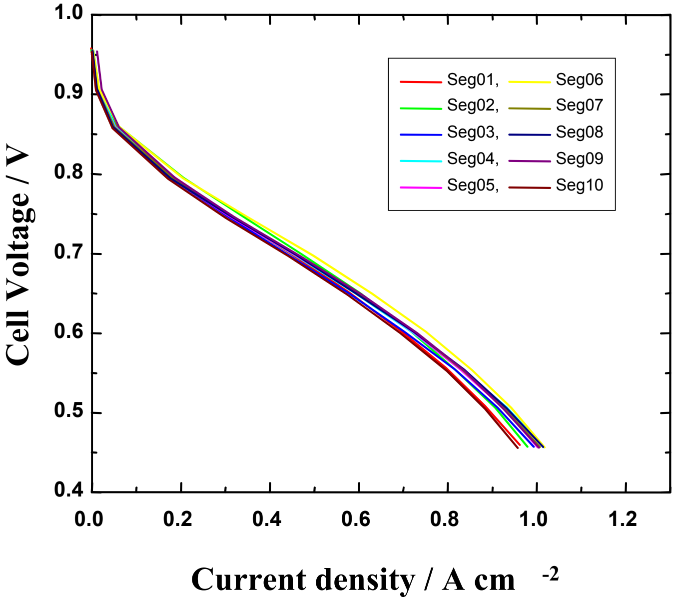


Cathode side
Pt M-Line
(hand painted)



XRF Imaging and Segment Performance in the Segmented Cell





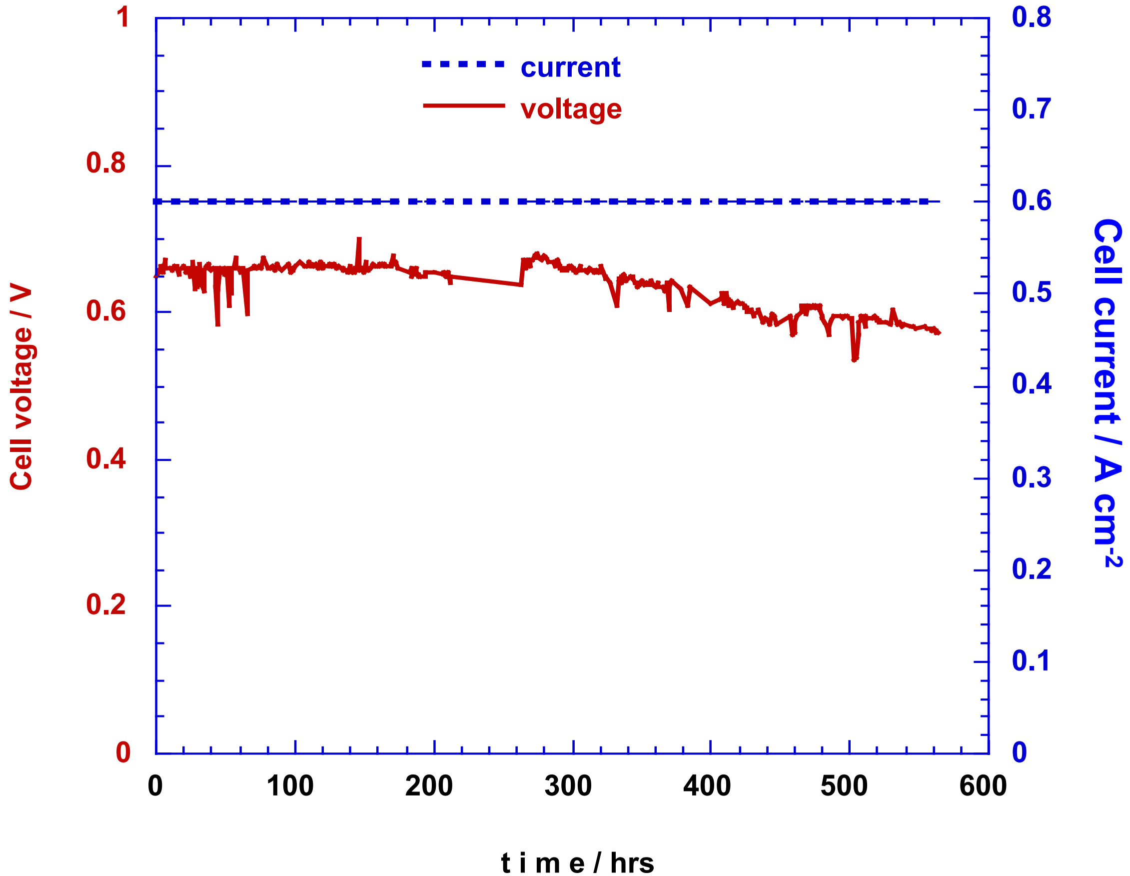
- Image shows even Pt distribution in all segments
- Even Pt distribution generates equivalent currents in all segments

Anode: 810 sccm H_2 , T_A=105°C, p=30psig

Cathode: 4000 sccm Air, T_C=80°C, p=30psig

Cell temp. = 80°C, 0.2 mg Pt/cm^2 at each electrode

Pt:Cr / 3:1 alloy cathode catalyst performance and stability



Pt/Cr mass ratio changes (from XRF data)

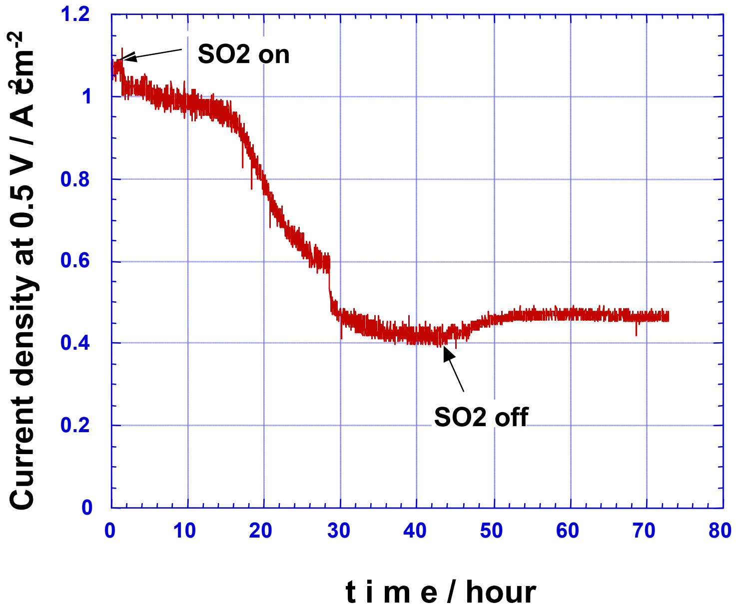
Initial: 0.053
Final: 0.042

Performance losses: 90 mV

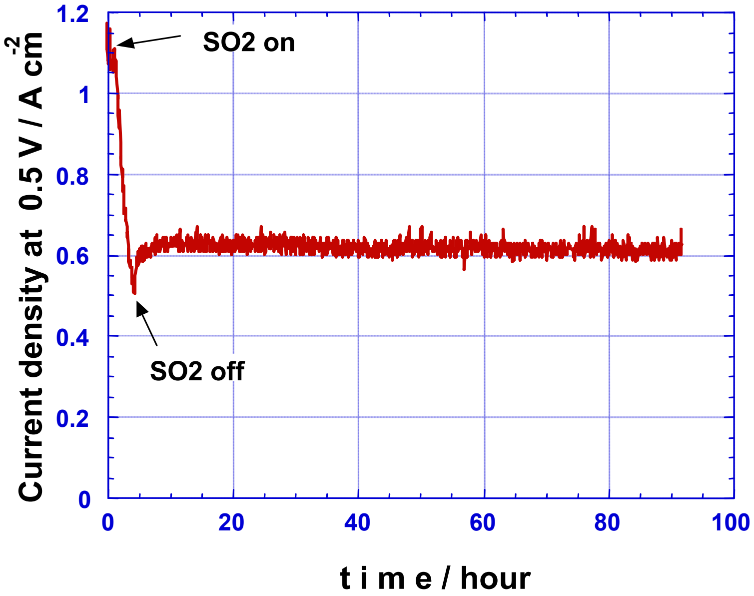
50 cm^2, 80 ^oC
A: 0.17 mg Pt cm^{-2} ;
C: 0.17 mg Pt/cm^{-2} (Pt_3Cr)
H_2:1.3 stoich; Air:2.0 stoich

FC Performance on cathode exposure to SO_2

1 ppm SO_2



5 ppm SO_2



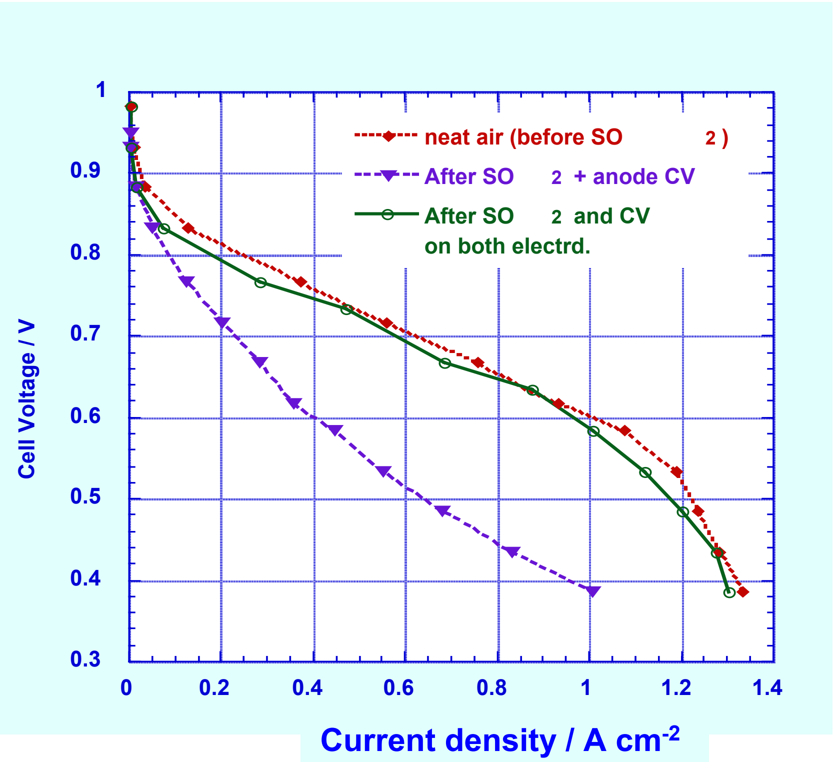
- Current became stable after 40 hr of operation
- FC performance did not recover much after SO_2 was shut off and cell run on clean air.

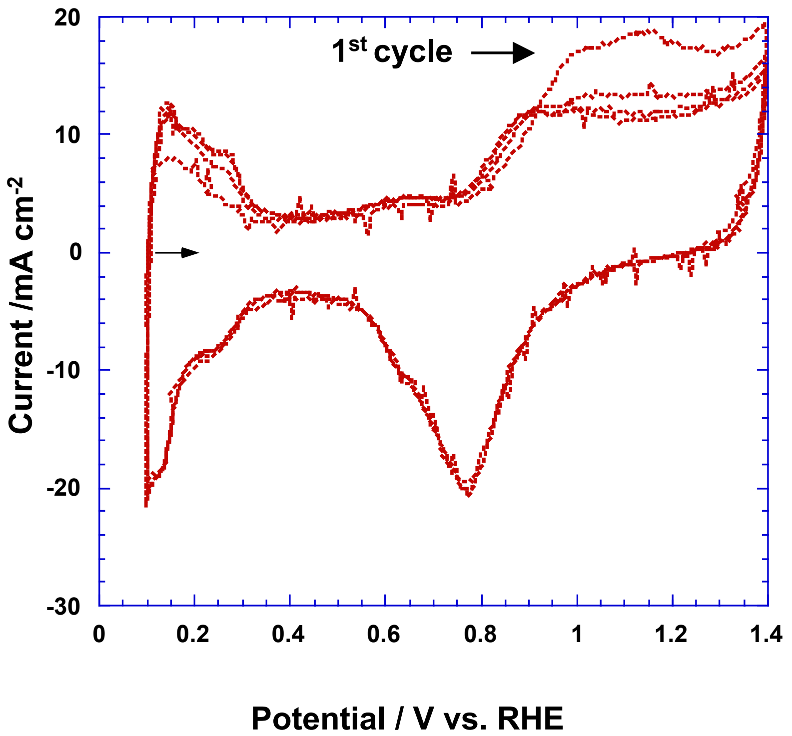
5 cm^2 H_2/air cell , T= 80 ^oC
A: 0.17 mg Pt/cm^{-2}
C: 0.18 mg Pt/cm^{-2}

- Cathode was exposed to SO_2 for 3.4 hr
- FC performance did not recover after SO_2 was shut off and cell run on clean air for 87 hr
- Degradation appears to be irreversible
- **Exposure to SO_2 must be avoided**

SO_2 Effect on FC Performance at 60° C and Cyclic Voltammetry at the cathode after poisoning

5 ppm SO_2 injected at the cathode

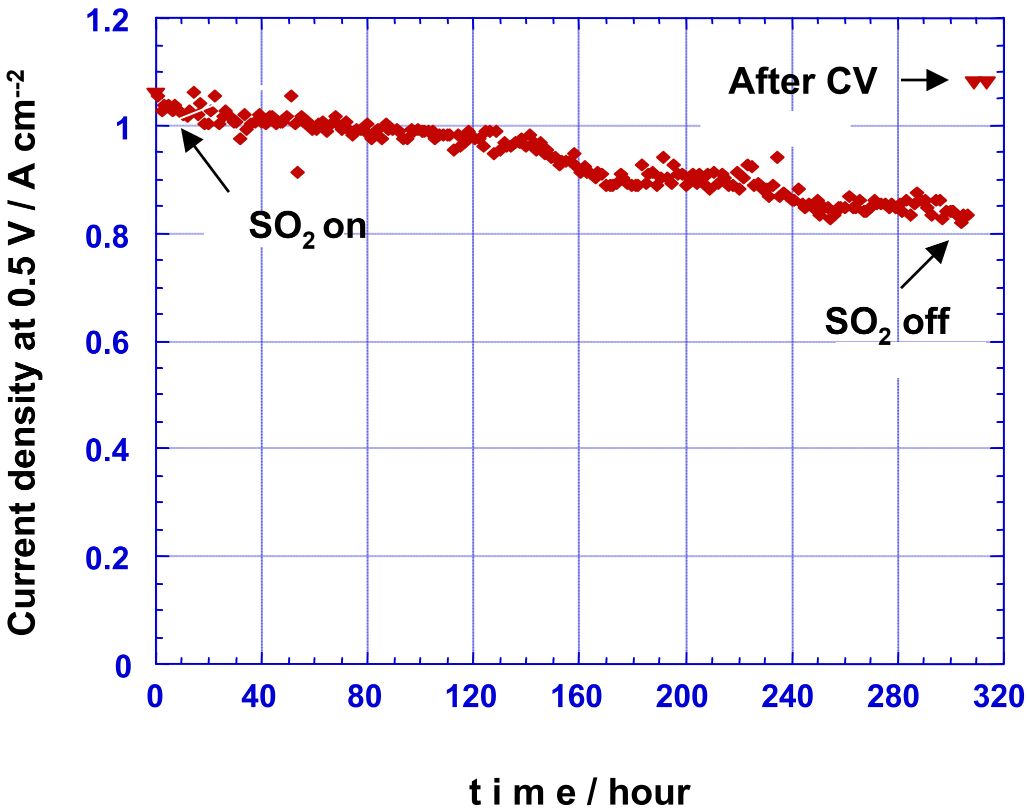




* **5 ppm SO_2 injected at the cathode for 17.6 hrs**
* **Decreased H_{ads} peaks reveals partial Pt surface poisoning by SO_2**
* **High potentials (>1 V) are required for cleaning the Pt surface**
* **After CV at the cathode, the cell recovered full performance**

5 cm^2 H_2/air cell , T= 60 °C
A :0.16 mg Pt/cm-^{2}
C: 0.19 mg Pt/cm^{-2}

Milestone: Life Test with 500 ppb SO_2 on the Cathode

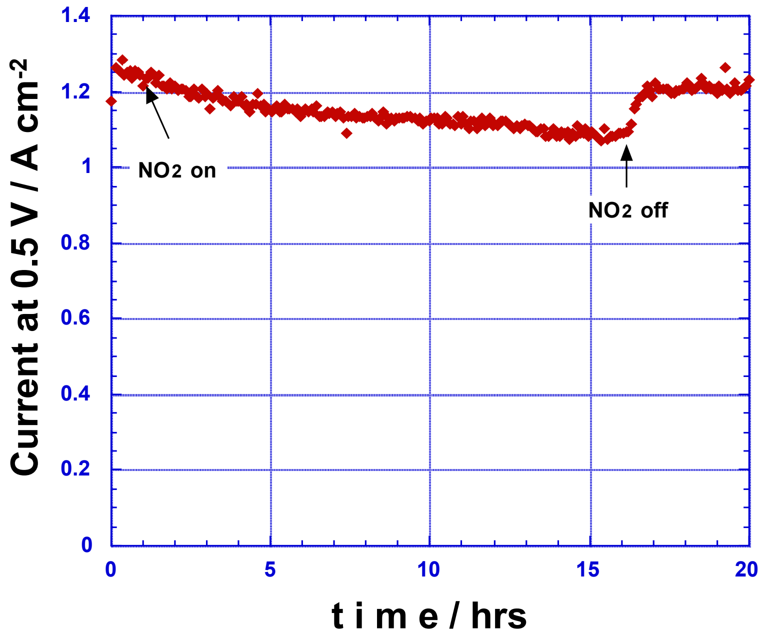


- Cell current dropped about 20 % during 300 hrs of exposure to SO_2
- Cell performance recovered after CV

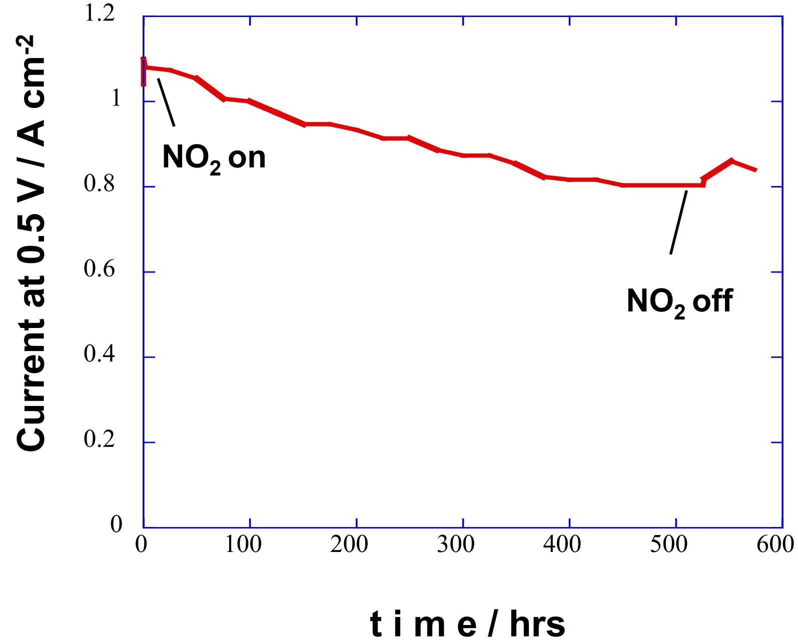
5 cm^2 H_2/air cell , T= 80 ^oC
A: 0.18 mg Pt/cm^2; 1.3 H_2 stoich
C: 0.22 mg Pt/cm^2; 2.5 air stoich
20% Pt/C ETEK, N1135

Effect of NO_2 on Cathode FC Performance

5 ppm NO_2



400 ppb NO_2



* 5 ppm NO_2 injected at the cathode along with the air
* NO_2 has a detrimental effect on FC performance
* The cell fully recovered on operation with clean air

* NO_2 injected at the cathode for 500 hr.
- Cell did not recover performance after NO_2 was turned off and operated on clean air for approximately 70 hrs

5 cm^2 H_2/air cell , T= 80 ^oC
A: 0.23 mg Pt/cm^2
C: 0.23 mg Pt/cm^2

Technical Progress Summary/Findings

General

* FC performance and catalyst layer porosity correlates with Nafion content.
* Pt catalyst contents and distribution in the MEA can be determined by XRF imaging.

Anode

* Modest progress to CO tolerance with RCA, but 500 ppm CO target not achieved yet.
* Low Pt content BNL catalyst tested for 222 hours. Performance decreased with time.
* Foreign cations decrease the ionic conductivity of the catalyst layer.

Cathode

* Operation at high voltages degrades performance due to Pt surface oxidation.
* PPB levels of SO_2 and NO_2 in the air stream degrades cathode performance.
* Negative effects of SO_2 are irreversible under normal FC operating conditions.
* A SO_2-poisoned catalyst cannot be reactivated with neat air.
* Cell recovery on exposure to NO_2 depends on concentration and time of exposure.
* Short term (1 hr) cathode exposure to NaCl solutions only affect air transport (flooding).

Future Work

General

1. **Develop methods for cleaning or reactivating poisoned catalysts** (e.g. H_2S and SO_2) **under standard operating conditions**
2. **Initiate studies on effects of impurities and conditions on gas diffusion layer**

Anode

1. **Test new BNL catalyst** (2% Pt / 20% Ru/C)
2. **Examine CO tolerance of BNL catalysts in reconfigured anodes** (RCA)
3. **Elucidate CO oxidation mechanism in RCA**
4. **Model impurity effects**

Cathode

1. **Evaluate new catalyst materials** (high Pt content)
2. **Study tolerance to SO_2 and NO_2 with filters**
3. **Determine poisoning mechanism by NO_2**
4. **Study simultaneous tolerance to SO_2 and NO_2 with filter**
5. **Investigate the effect of NaCl and $CaCl_2$ on cathode performance**
6. **Study the effect of particulate matter from the air on FC performance**
7. **Initiate non-precious metal based catalysts studies**