Effects of Impurities on Fuel Cell Performance and Durability

Project ID#: FCP16

James G. Goodwin, Jr., Jack Zhang, Kitiya Hongsirikarn, and Zhiming Liu

Clemson University

William Rhodes, Hector Colon-Mercado

Savannah River National Lab

Peter Finamoore

John Deere, Advanced Energy Systems Division

Overview

- **Timeline**
  - Start: Feb. 15, 2007
  - Finish: Feb. 14, 2011
  - Completed: 3 %
- **Budget**
  - Total Project Funding
    - DOE Share:
      - CU: $1,205,425
      - SRNL: $774,979
    - Cost Share:
      - CU: $295,101
      - John Deere: $193,745
  - Funding received in FY07 (as of 4/19/07)
    - CU: $100,000
    - SRNL: $125,000
  - Funding for FY08
    - CU: $295,721
    - SRNL: $193,866
  - Funding reduced - None
- **Barriers**
  - None anticipated
- **Targets**
  - Measurement of effects of gas impurities on fuel cell (FC) components (Pt, Nafion)
  - Correlation of changes in performance characteristics of FC to measured effects
  - Proposed mechanisms for impurity effects
  - Development of strategies to reduce impact of impurities
- **Partners**
  - Clemson University
  - SRNL
  - John Deere

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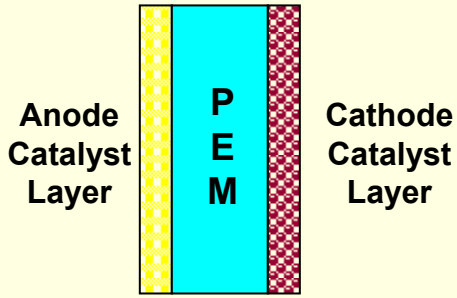
Background

Fuel Cell Structure



Membrane Exchange Assembly

Anode:	$H_2 - 2e \rightarrow 2H^+$	(1)
Cathode:	$\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$	(2)
Overall:	$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$	(3)

Impurities in the gas streams to a FC can result in a decrease in FC performance due to poisoning of the Pt catalyst and adsorption (and blockage) of the Bronsted acid sites of the Nafion which interfers with its ability to shuttle protons.

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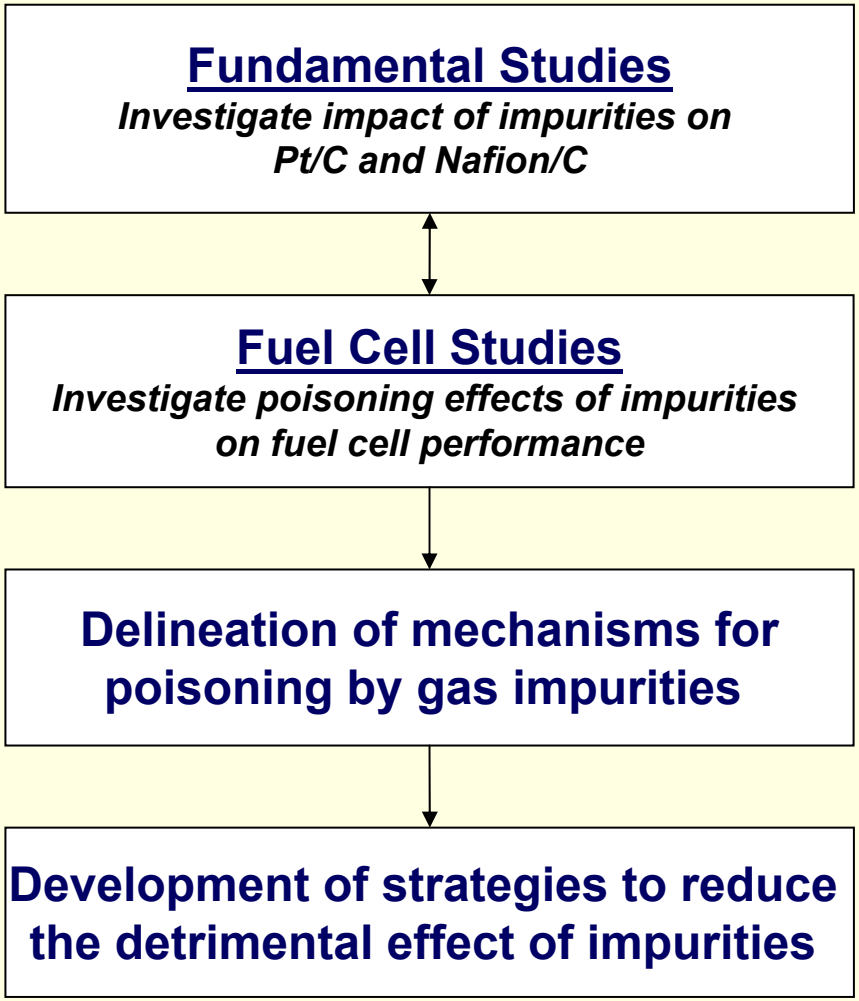
Research Plan



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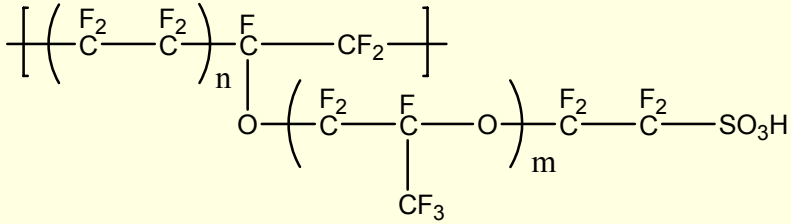
Experimental: Materials*

- **Anode: 20 wt% Pt/C (E-TEK)**
  - **Pt Particle Size: 22 Å**
  - **BET Surface Area: 128 m^2/g**
- **<u>Cathode: 40 wt% Pt/C (E-TEK)</u>**
  - ***Pt Particle Size: 29 Å**
  - ***BET Surface Area: 100 m^2/g**
- **5 wt% Nafion EW 1100 Solution (Ion-Power)**



- **Carbon Black Powder (XC-72R)**
  - **BET Surface Area: 250 m^2/g**
- **MEAs (E-TEK)**
- **Nafion ® 211 Membrane EW 1100 (Du Pont)**

** Commercial Products*

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Experimental: Fund. Characterization

- **Pt/C, Pt-Nafion/C**
  - BET
  - XRD
  - SEM/TEM
  - EDS
  - FT-IR
  - Eff. of Impurities on H_2 Adsorption
  - Eff. of Impurities on Reaction
    - *H_2-D_2*
    - *H_2-O_2*
- **Nafion**
  - Impedance analysis
- **Nafion/C, Pt-Nafion/C**
  - BET
  - SEM
  - EDS
  - Acid site titration
  - NH_3 adsorption
    - *Eff. of Impurities on Bronsted sites*
  - FT-IR
  - Model acid-catalyzed reaction
    - *Eff. of impurities on Bronsted sites*

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Experimental: Impurities to be Studied

- CO and NH_3
- H_2O, O_2, CO_2
- Hydrocarbons
- He, N_2, Ar
- Sulfur-containing gases
- Halogenated compounds
- Particulates

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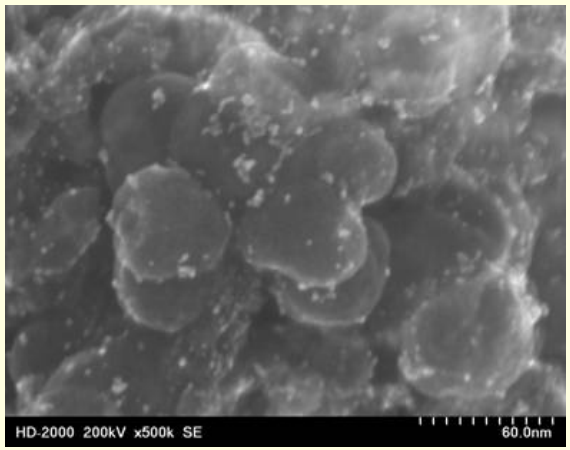
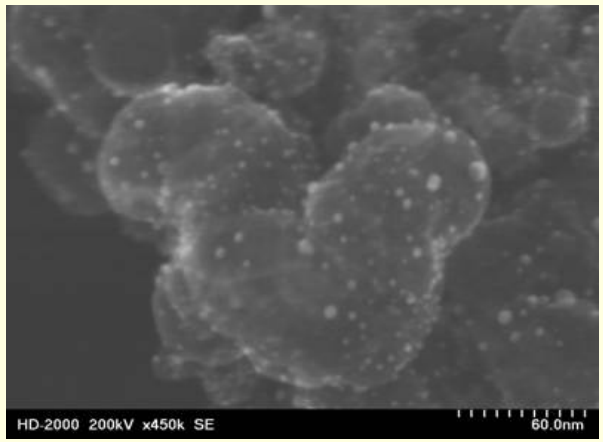
Results: 20 wt% Pt/C

- **BET Surface Area: 112 m^2/g**
- **SEM:**

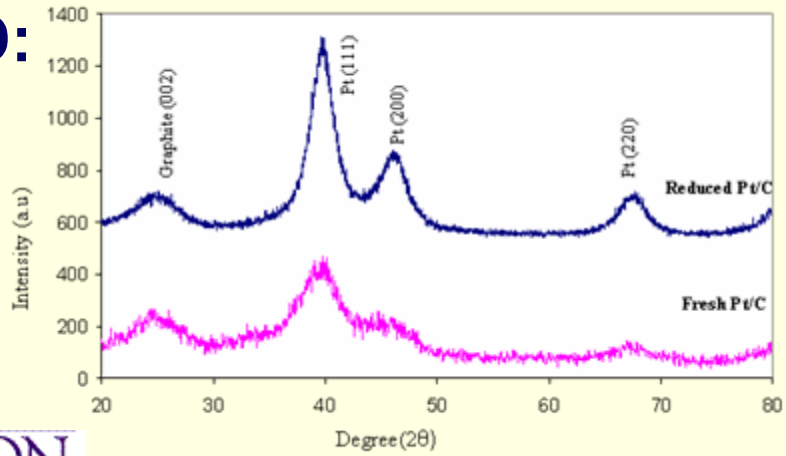


Fresh Pt/C



Reduced Pt/C

- **XRD:**



On the fresh Pt/C catalyst, the Pt particles are highly dispersed. During reduction, some aggregation of the Pt particles occurs.

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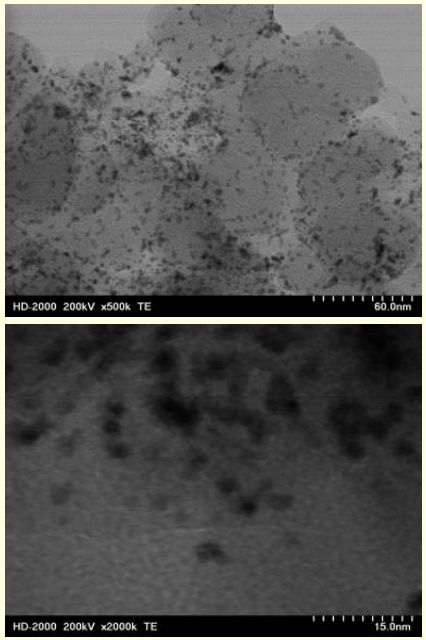
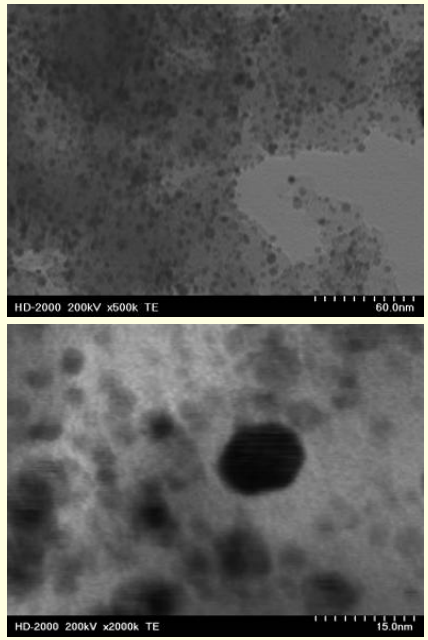
Results: 20 wt% Pt/C

- **TEM:**

Fresh Pt/C



Reduced Pt/C



On the reduced Pt/C catalyst, Pt particles aggregate and form larger particles.

On the fresh Pt/C catalyst, Pt particle sizes are about 1-2 nm, compared to 10 nm on the reduced Pt/C catalyst.

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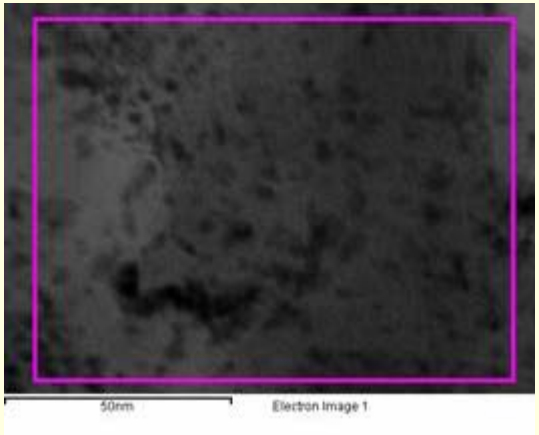
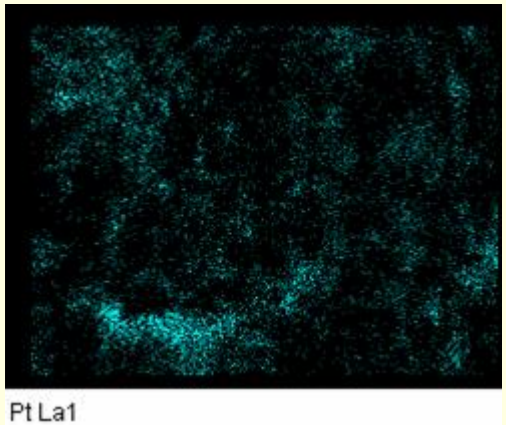
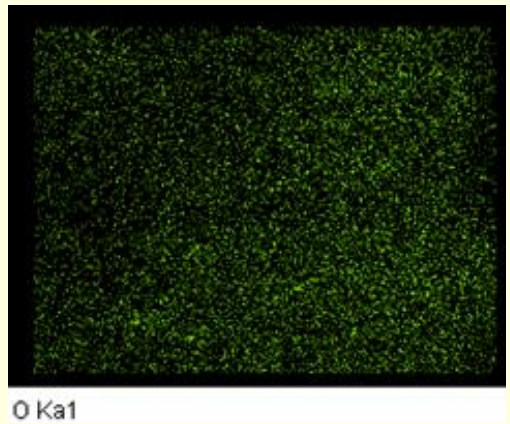
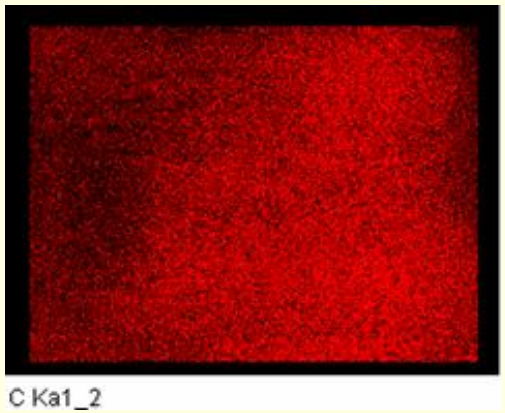
Results: 20 wt% Pt/C

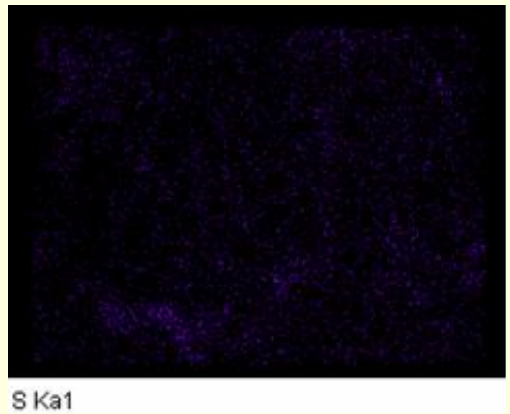
- **EDS-Fresh Pt/C:**




Pt La1


O Ka1


C Ka1_2


S Ka1

EDS showed that Pt, O, C and a small amount of S are present in fresh Pt/C.

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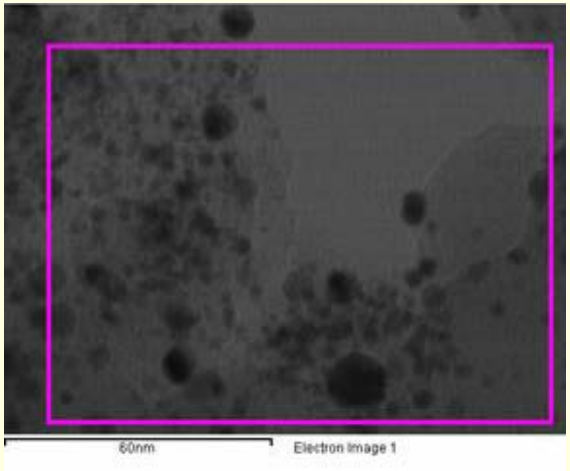
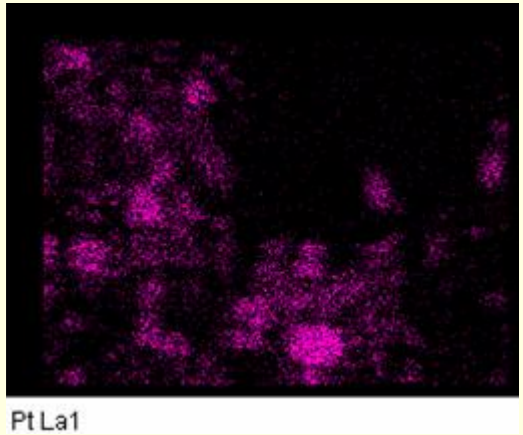
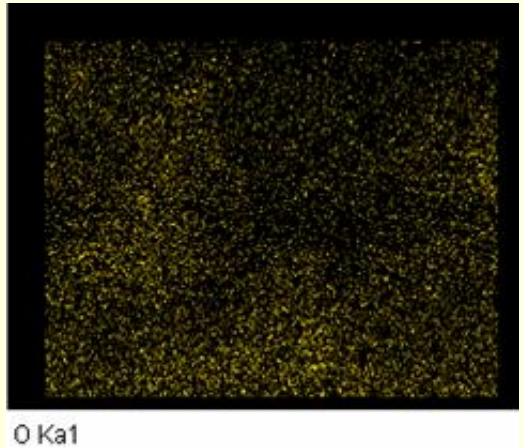
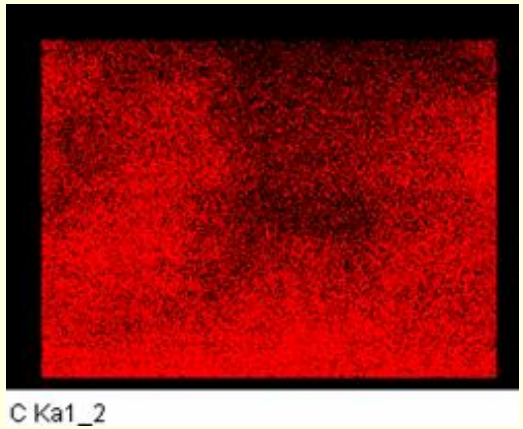
Results: 20 wt% Pt/C

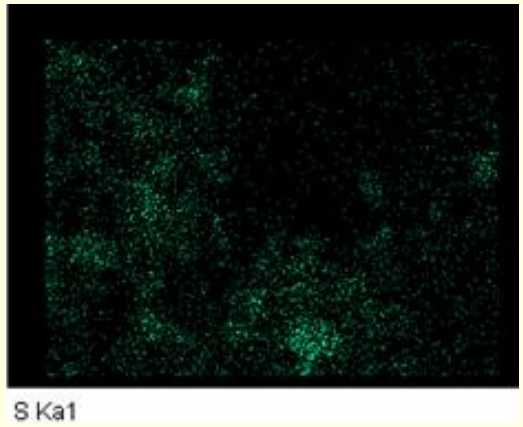
- **EDS-Reduced Pt/C:**











O, C and S are also present on the reduced Pt/C.

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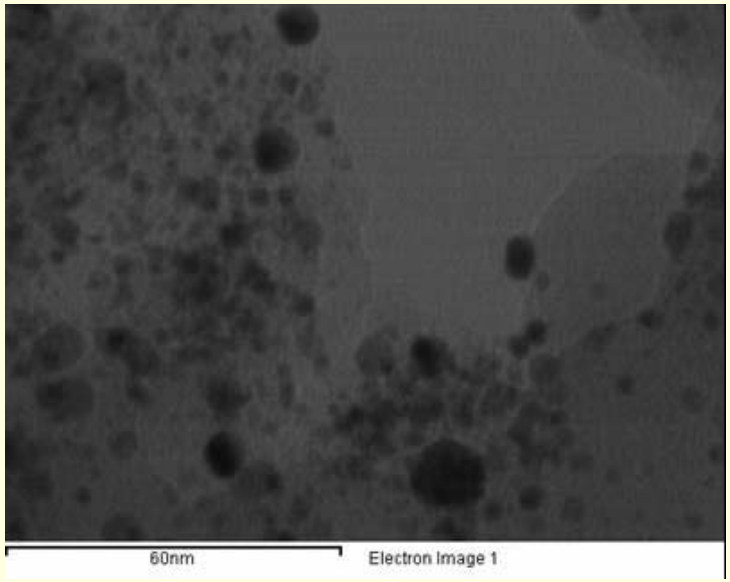
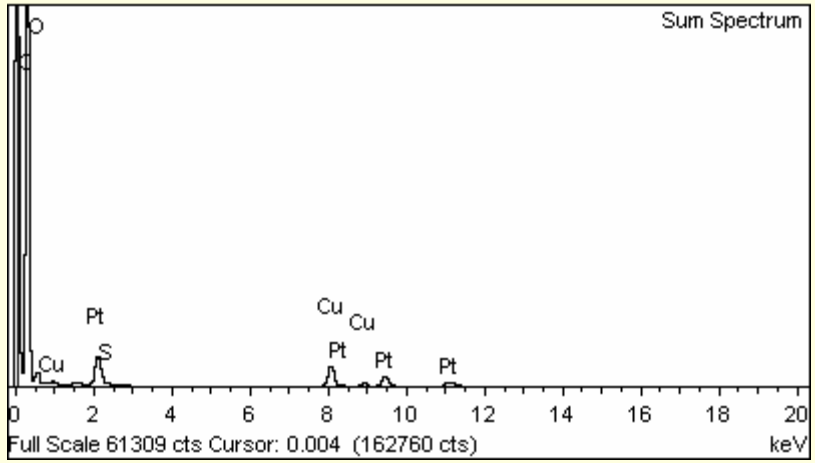
Results: 20 wt% Pt/C

- **EDS-Reduced Pt/C:**





Element	Wt. %	Atom. %
C K	84.8	96.8
O K	2.5	2.1
S K	0.4	0.2
Pt M	12.4	0.8
Total	**100**	**100**

The amount of S on the reduced Pt/C is also small.

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Results: Nafion/C

- **BET Surface Area:**
  - Carbon Support: 226 m^2/g
  - 23 wt% Nafion/C: 81 m^2/g
- **Acid Site Density:**
  - 30 wt% Nafion/C: 186 ± 6 µmol/g
- **EDS**
  - *EDS mapping showed that the Nafion ionomer was uniformly dispersed on the carbon support.*

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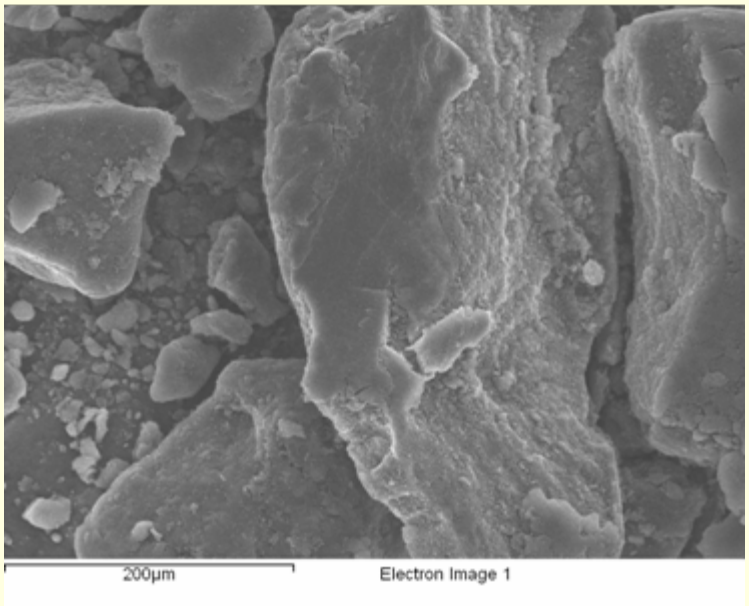
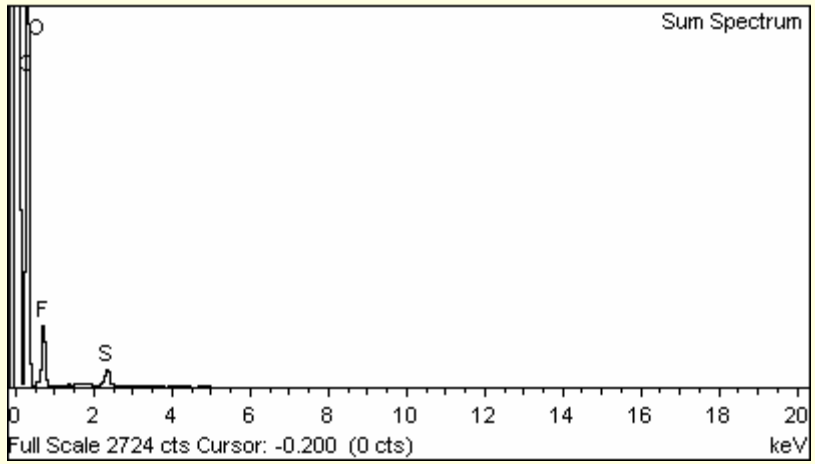
Results: Nafion/C

- **EDS:**



23% Naf/C



Element	Weight%	Atomic%
C K	74.7	82.2
O K	3.6	3.0
F K	20.7	14.4
S K	1.0	0.40
Totals	100.00	

EDS of 23 wt% and 30 wt% Nafion/C indicated that there are no significant impurities.

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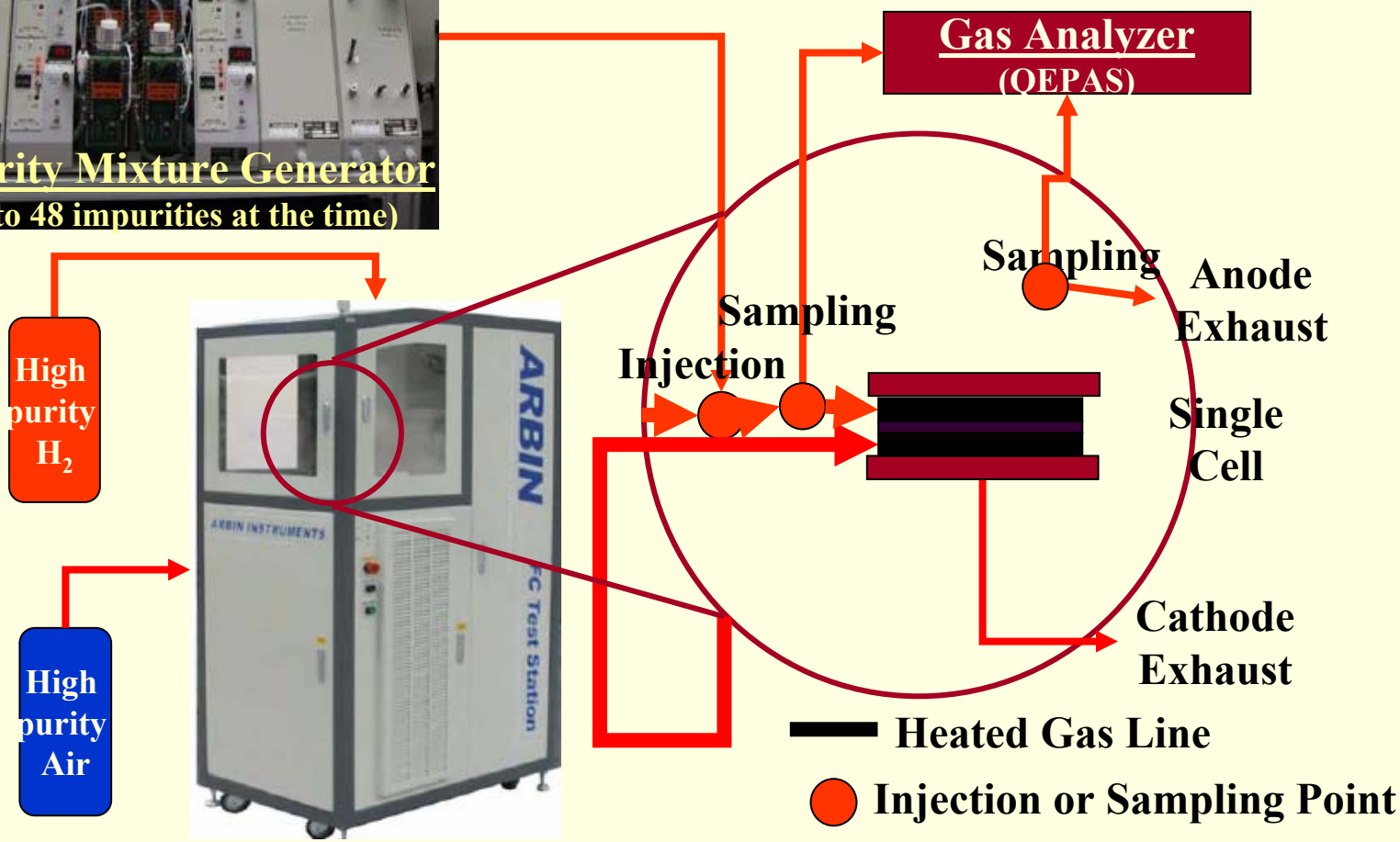
Fuel Cell Studies: Test Equipment

Impurity Mixture Generator
(Up to 48 impurities at the time)

SRNL Test Equipment



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Fuel Cell Studies: Equipment

- **FC Single Cell Test Station**
  - *Arbin FCTS 200H*
    - *Max. Power: 200 W*
    - *Max. Temp.: 130°C*
- **Electrochemical System**
  - *PARSTAT 2273*
    - *Max. Current: 2 A*
    - *EIS capability*
- **Gas Impurity Mixture Generator**
  - *Kin-Tek mixture generator*
    - *Up to 48 mixed impurities*
    - *Up to 500 sccm*
- **Gas Analyzer**
  - *Quartz-Enhanced Photoacoustic Spectrometer (QEPAS)*
    - *PPM sensitivity*

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Fuel Cell Studies: Test Matrix 2007

Temperatures	**80° C**
Pressures	**2 bara(P_a=P_c)**
Humidity	**100 % RH anode** **50 % RH cathode**
Stoichiometry (A/C)	**1.1/2.5 @ 1000 mA/cm^2** **H_2/Air**
Loading	**Anode 0.1 mg Pt/cm^2 (20 wt% Pt-C)**
	Cathode 0.3 mg Pt/cm^2 (40 wt% Pt-C)
Electrolyte	**Nafion® 211**
Cell Area	**50 cm^2**
Current density	**1000 mA/cm^2**

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Fuel Cell Studies: Contaminant Eval. 2007

- Evaluation will concentrate on NH_3
- Contaminant Survey (100 h test)
  - At constant current, start with lowest concentration and periodically increase the concentration until 10% voltage drop is achieved.
  - Performance (V-I) is evaluated every 10 h.
  - Recovery is assessed.
  - Dosage is calculated.
- Long term (400 h test)
  - Contaminant concentration from Survey that yields 10% voltage drop at the end of 400 hours is selected.
- Impedance change as a function of time
- Cyclic Voltammetry at the beginning and end of experiments
- Post mortem analysis (SEM, TEM, Electronmicroprobe, XPS)

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Future Work (FY07-FY08)

Activities

- Purchase fuel cell materials (Pt/C, Nafion ink, Nafion membranes) and equipment (FT-IR, Impedance Analyzer, Fuel Cell Station).
- Prepare materials for fundamental studies.
- Develop protocols for fundamental studies mimicking fuel cell conditions.
- Study effect of CO and NH_3 on properties of Pt/C, Nafion/C, Pt+Nafion/C, and Nafion membranes.
- Develop protocols for fuel cell studies.
- Investigate the effect of CO, NH_3, and CO_2 on fuel cell performance.

Upcoming Milestones

- Complete fundamental study of effect of CO on Pt/C and Pt+Nafion/C.
- Complete fundamental study of NH_3 on Nafion/C, and Nafion membrane.
- Complete study of effect of CO, NH_3, and CO_2 on fuel cell performance.

Decision Points

- None in FY07-FY08.

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Summary

- Project started in Feb. 2007.
- MEA materials have been purchased.
- Characterization studies have begun for:
  - Pt/C
  - Nafion/C
  - Pt-Nafion/C
- Equipment has been ordered:
  - FT-IR
  - Impedance Analyzer
  - Fuel Cell Station

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