An Overview of Montana State University HiTEC Research Activities

Lee H. Spangler, Director MSU-HiTEC

HiTEC (the High Temperature Electrochemistry Center) is a collaborative center between Montana State University and Pacific Northwest National Laboratory

MSU Personnel:

Steve Shaw (EE)	Max Diebert (Chem Eng.)	Hongwei Gao (EE)
Dick Smith (Physics)	V. Gorokhovsky (Arcomac)	Yves Idzerda (Physics)
Hashem Nehrir (EE)	Hugo Schmidt (Physics)	Lee Spangler (Chem)

PNNL Personnel:

G. Yang	O. Marina	P. Reike
G. McVay	L. Pederson	M. Khaleel
V. Shutthanandan (EMSL)	D. Gelles (EMSL)	

Outline

- Dynamic models of FC for DG studies
- Novel Adaptive power control scheme
- Large Area Filtered Arc Deposition coating technology for interconnects
- Materials characterization of coatings
- Area Specific Resistance measurements of coated materials

Needs for Dynamic Model of FC

FCs don’t respond as fast as desired to electrical load transients, mainly due to their slow internal chemical reaction.

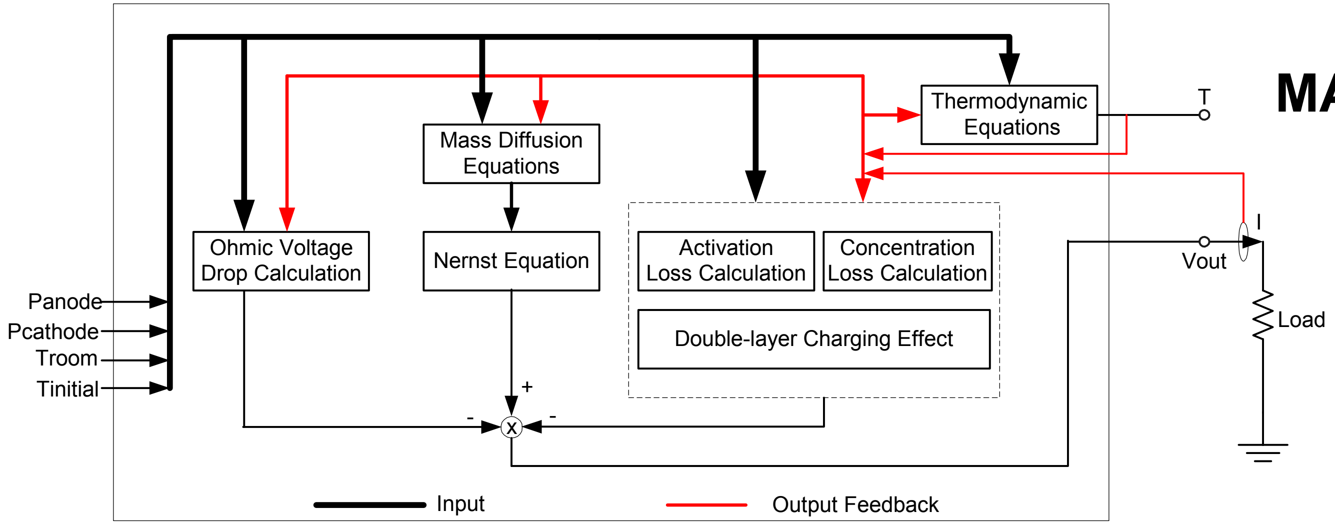
- Electrical load switching
- Motor starting

A dynamic model is needed in DG studies:

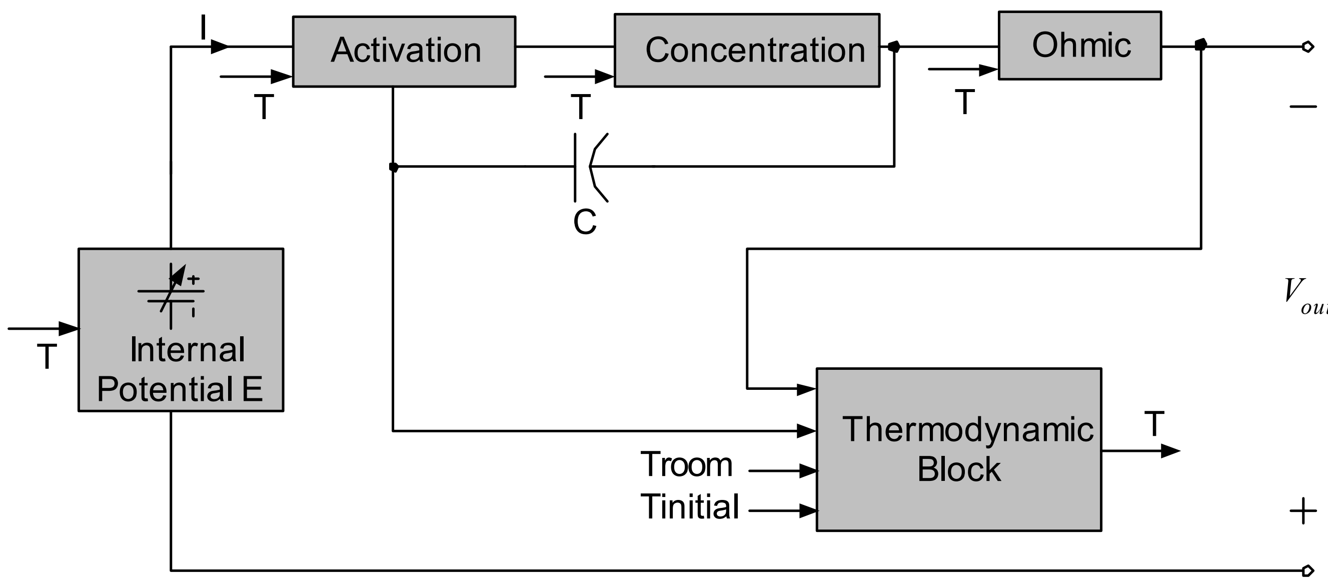
- FC dynamic performance under load transients
- Real-time control of FCs
- Power sharing in multi-source DG applications

Dynamic Models of Fuel Cells

MATLAB/SIMULINK

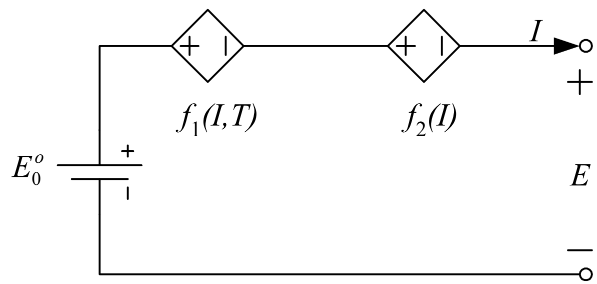


Pspice



Equivalent Electrical Circuits

Internal Potential E



$$f_1(I,T) = -\frac{N_{cell}RT}{2F}\ln\left[p^*_{H2}\cdot(p^*_{O2})^{0.5}\right] + N_{cell}k_E(T-298)$$

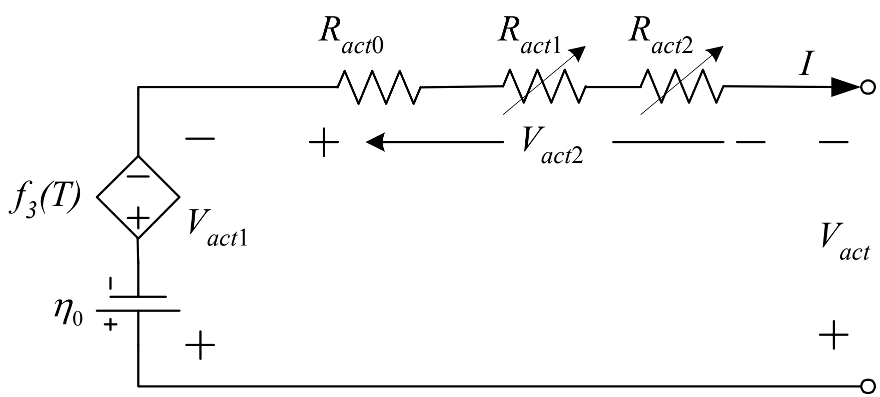
(p^*_{H2}, p^*_{O2} are functions of T and I.)

$$f_2(I) = N_{cell}E_{d,cell}$$

$$E_{d,cell}(s) = \lambda_e I(s)\frac{\tau_e s}{\tau_e s + 1}$$

(Fuel delay effect)

Activation



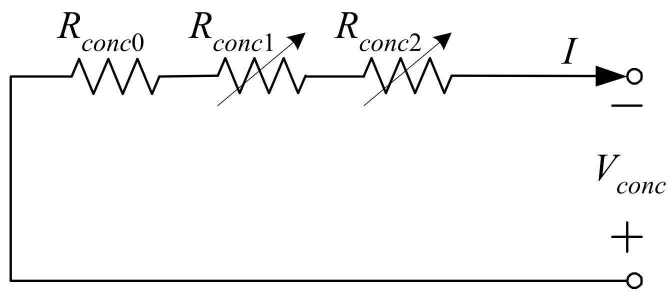
η_0: constant part of V_{act}

$$f_3(T) = (T-298)\cdot a$$

$$R_{act} = \frac{V_{act2}}{I} = R_{act0} + R_{act1} + R_{act2}$$

Equivalent Electrical Circuits (contd)

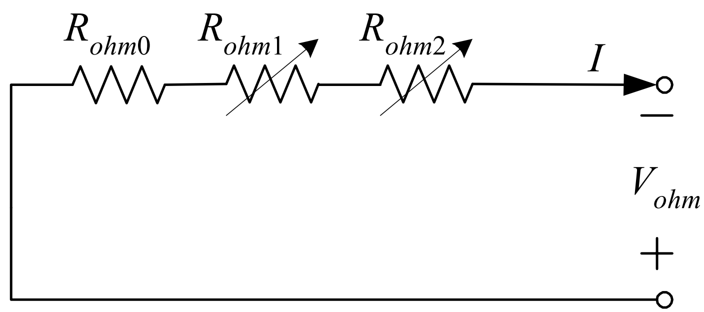
Concentration



$$R_{conc} = R_{conc0} + R_{conc1} + R_{conc2}$$

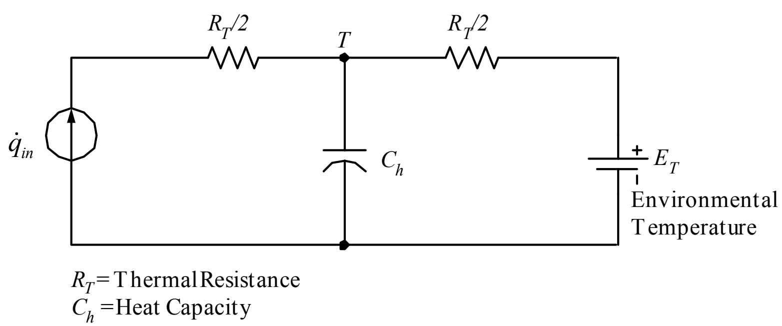
where *Rconc0* is the constant part of *Rconc* and *Rconc*1, *Rconc*2 are its current-dependent and temperature-dependent parts.

Ohmic



$$R_{ohm} = R_{ohm0} + R_{ohm1} + R_{ohm2}$$

Thermodynamic Block

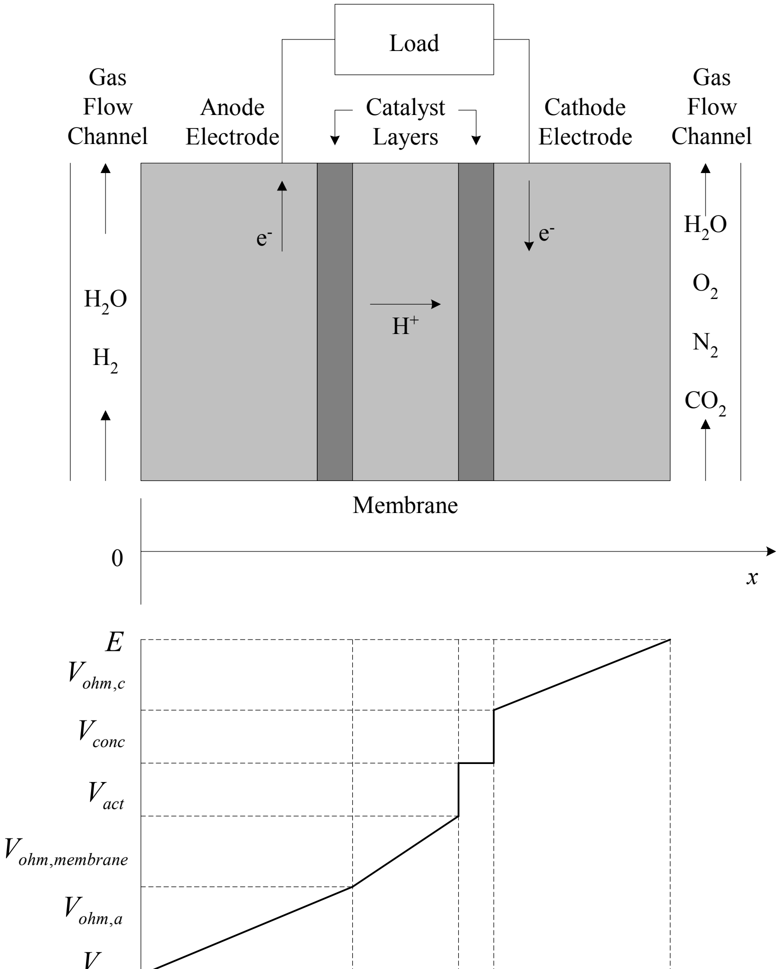


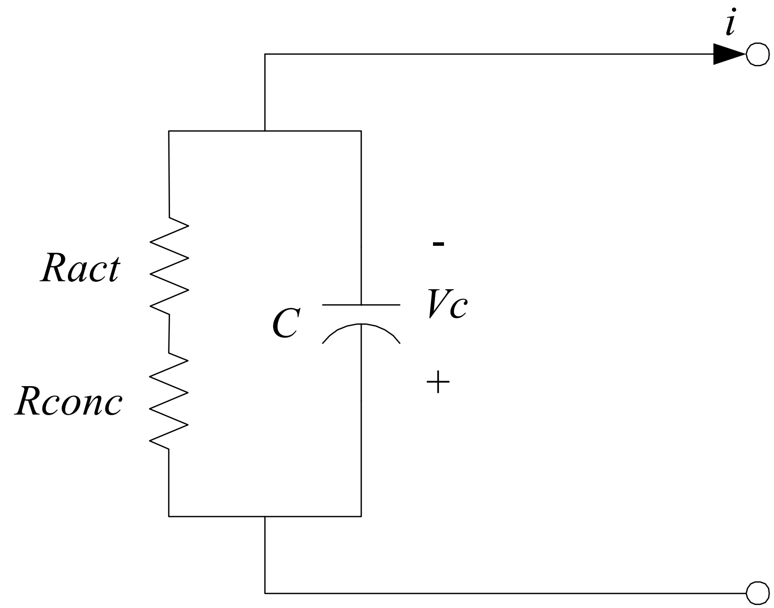
$$\dot{q}_{in} = (E - V_{out}) \cdot I$$

$$R_T = 1/(h_{cell} \cdot N_{cell} \cdot A_{cell})$$

The voltage across the capacitance (Ch) is the overall temperature of the fuel cell stack, T.

Equivalent Electrical Circuit of the Double-Layer Charging Effect

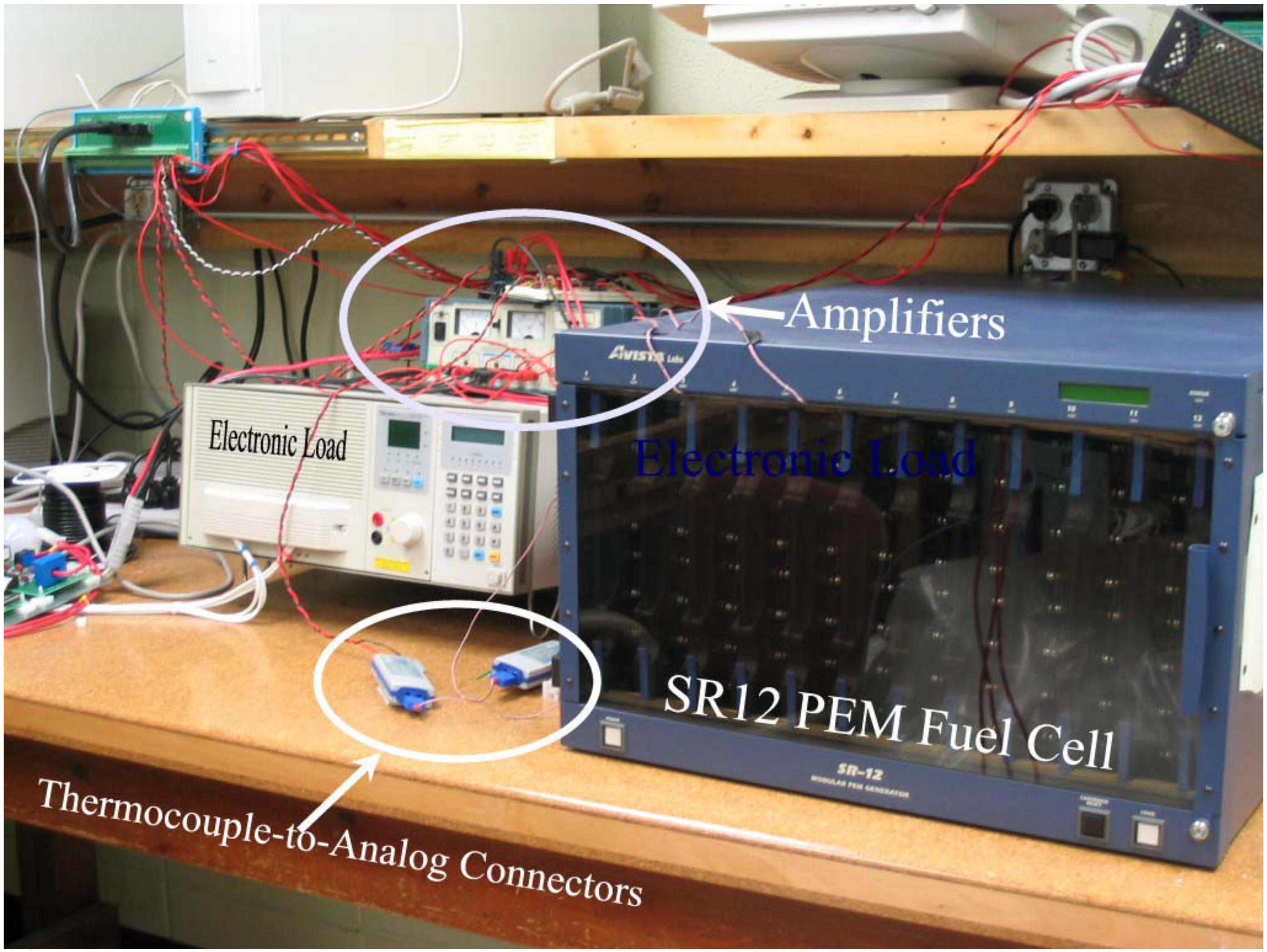




$$V_C = (i - C\frac{dV_C}{dt})(R_{act} + R_{conc})$$

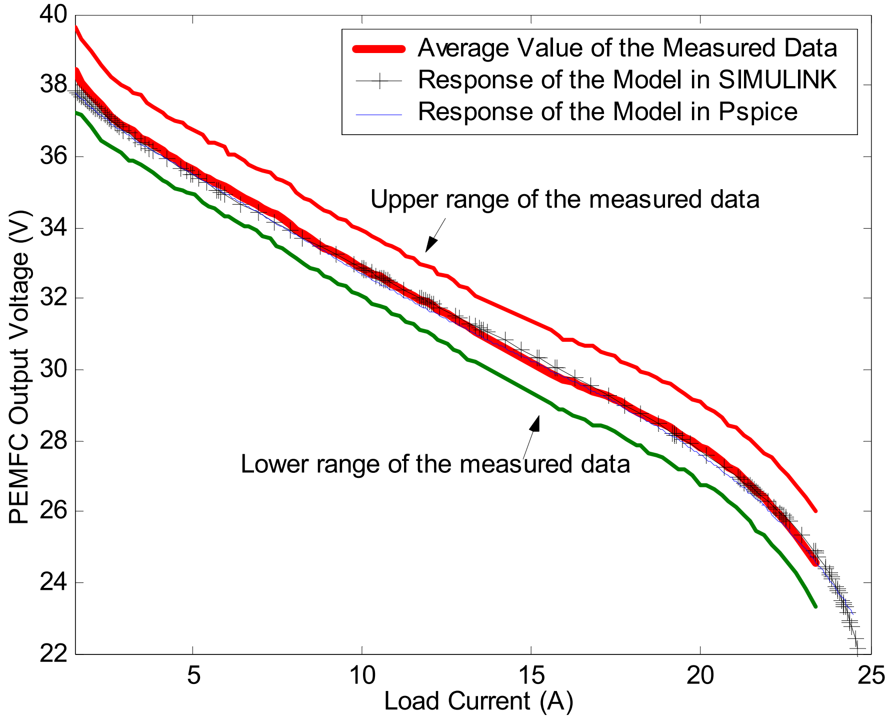
$$V_{outl} = E - V_C - V_{act1} - V_{ohm}$$

Model Validation for PEM FCs

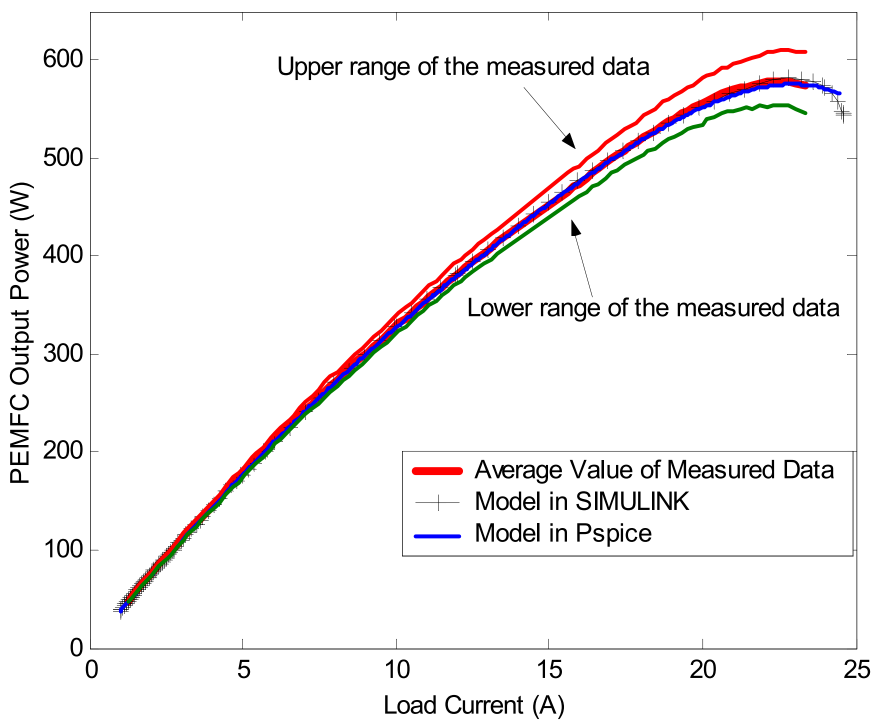


Simulation and Experimental Results:

PEMFC *Steady-state Response*



V-I Curve

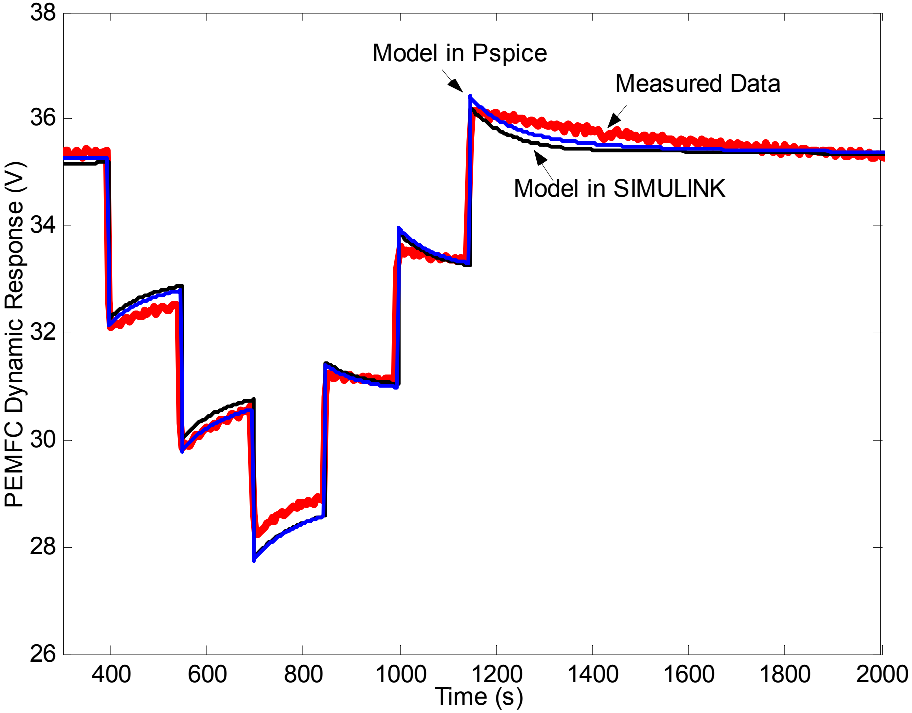


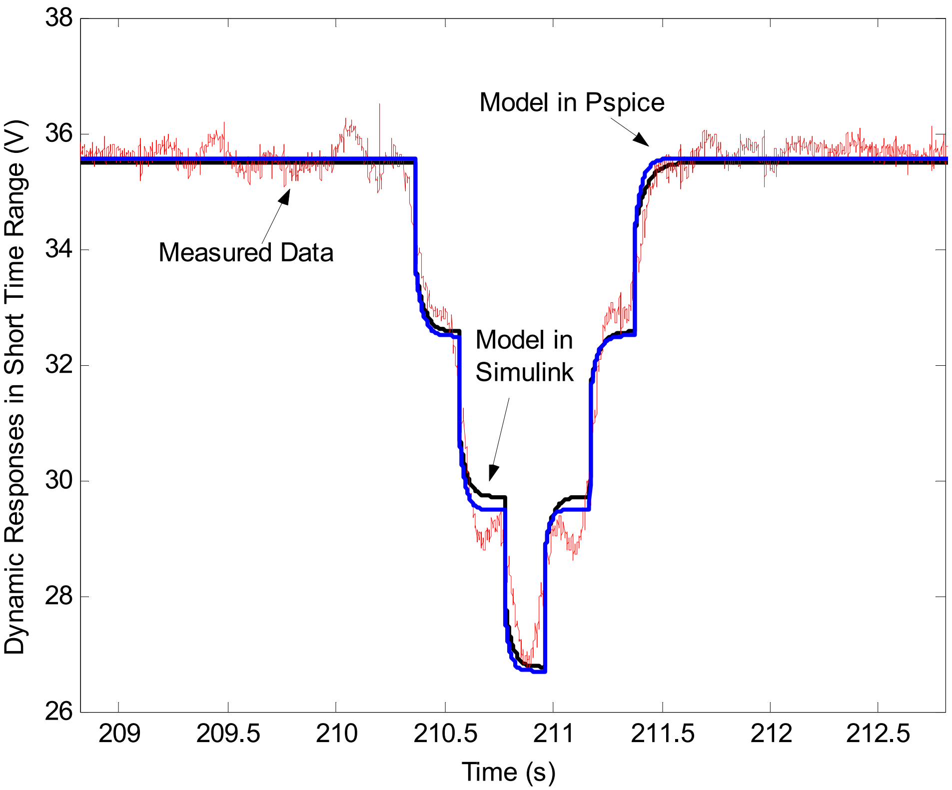
P-I Curve

Simulation and Experimental Results:

PEMFC Dynamic *Response*

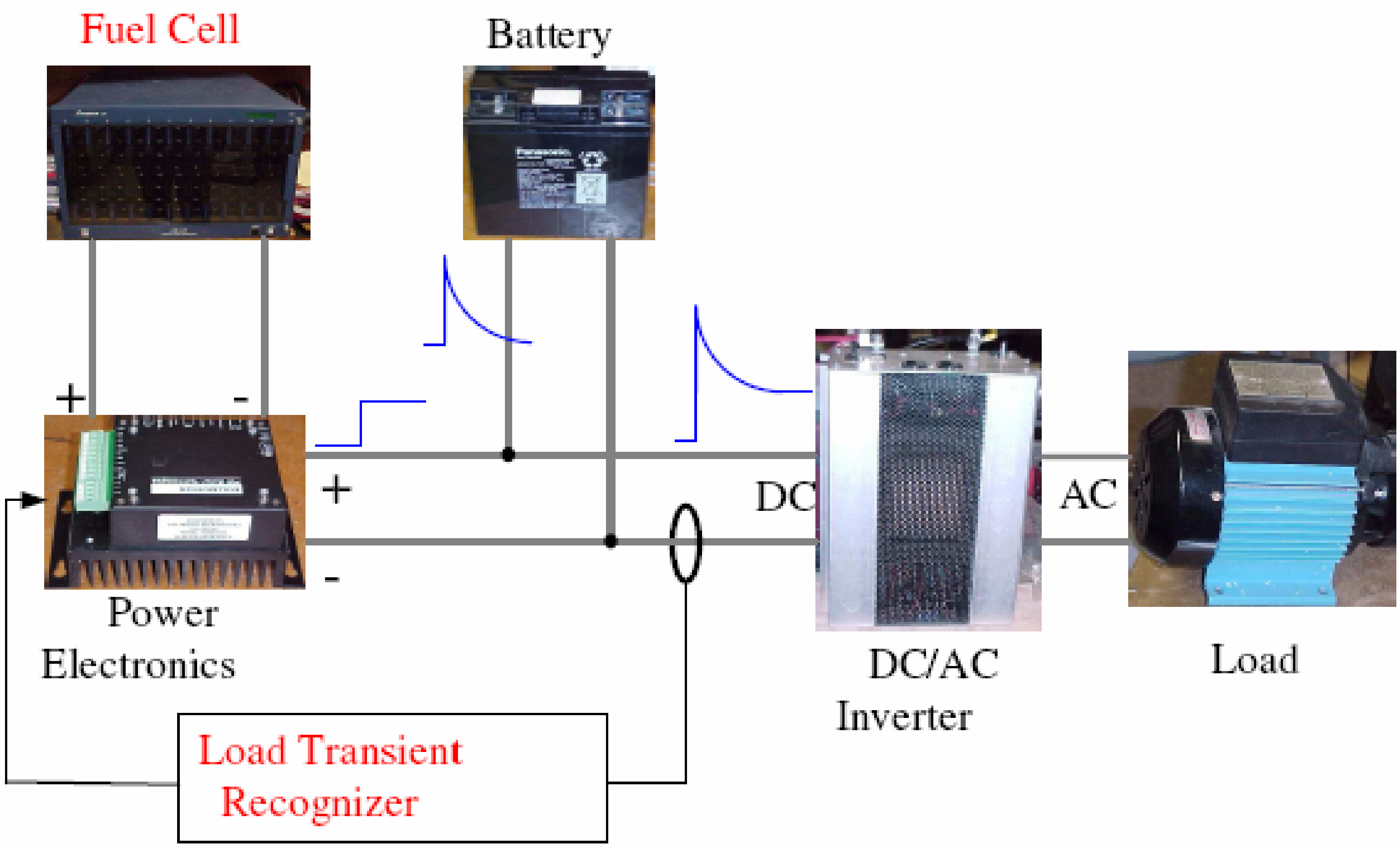
Transient responses of the models in long time range.



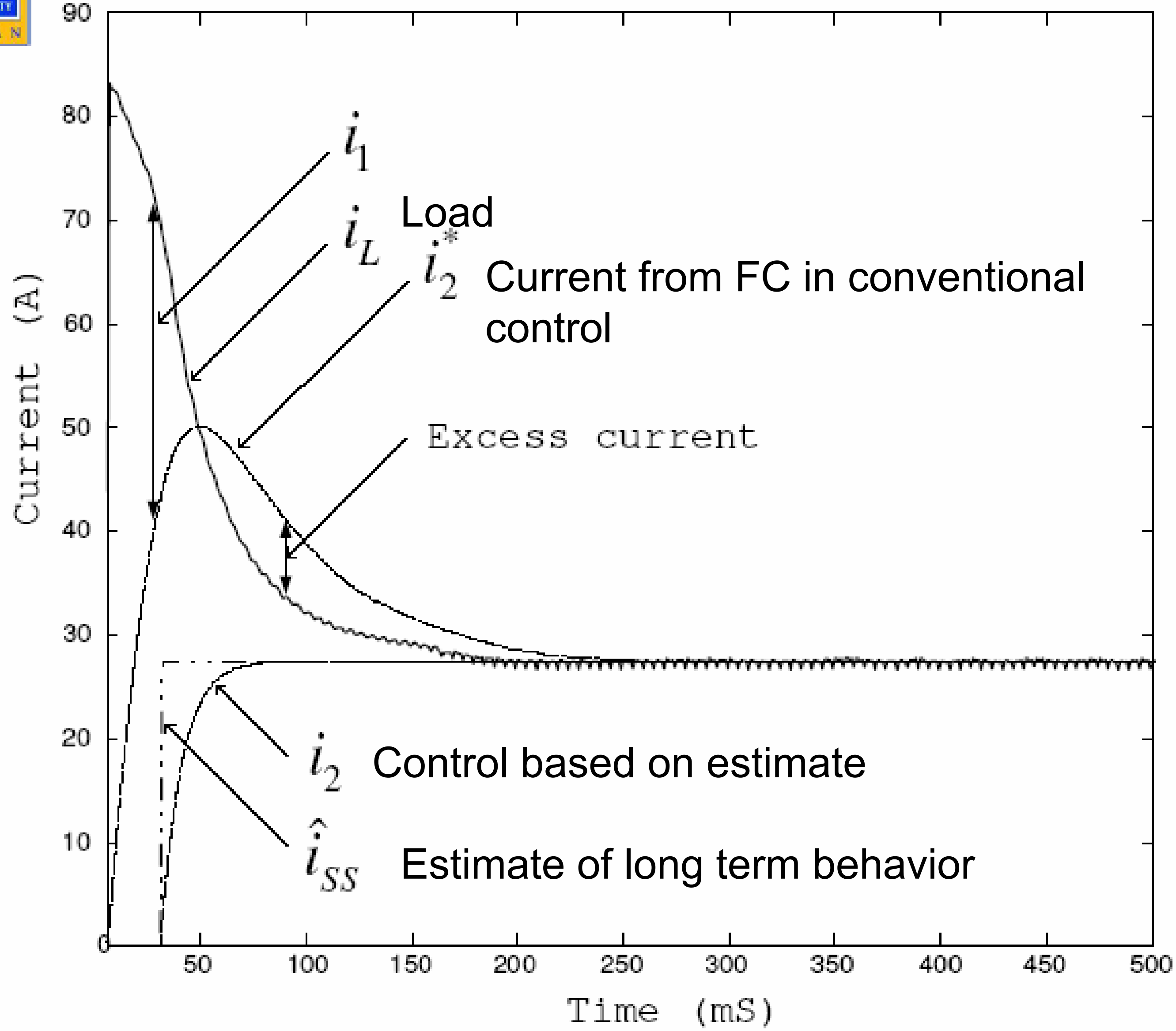


Transient responses of the models in short time range.

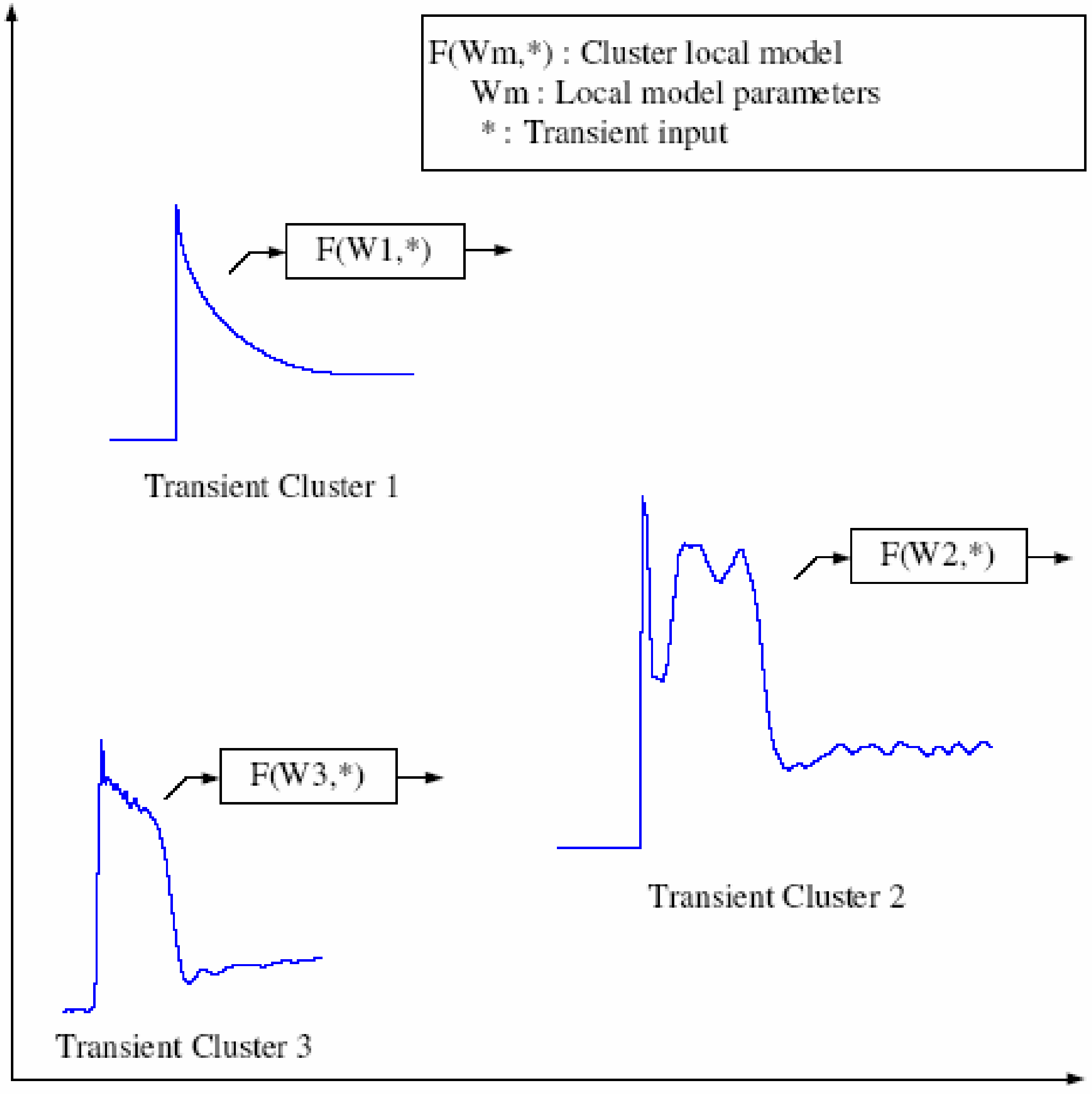
Multi-source Control Demonstration System



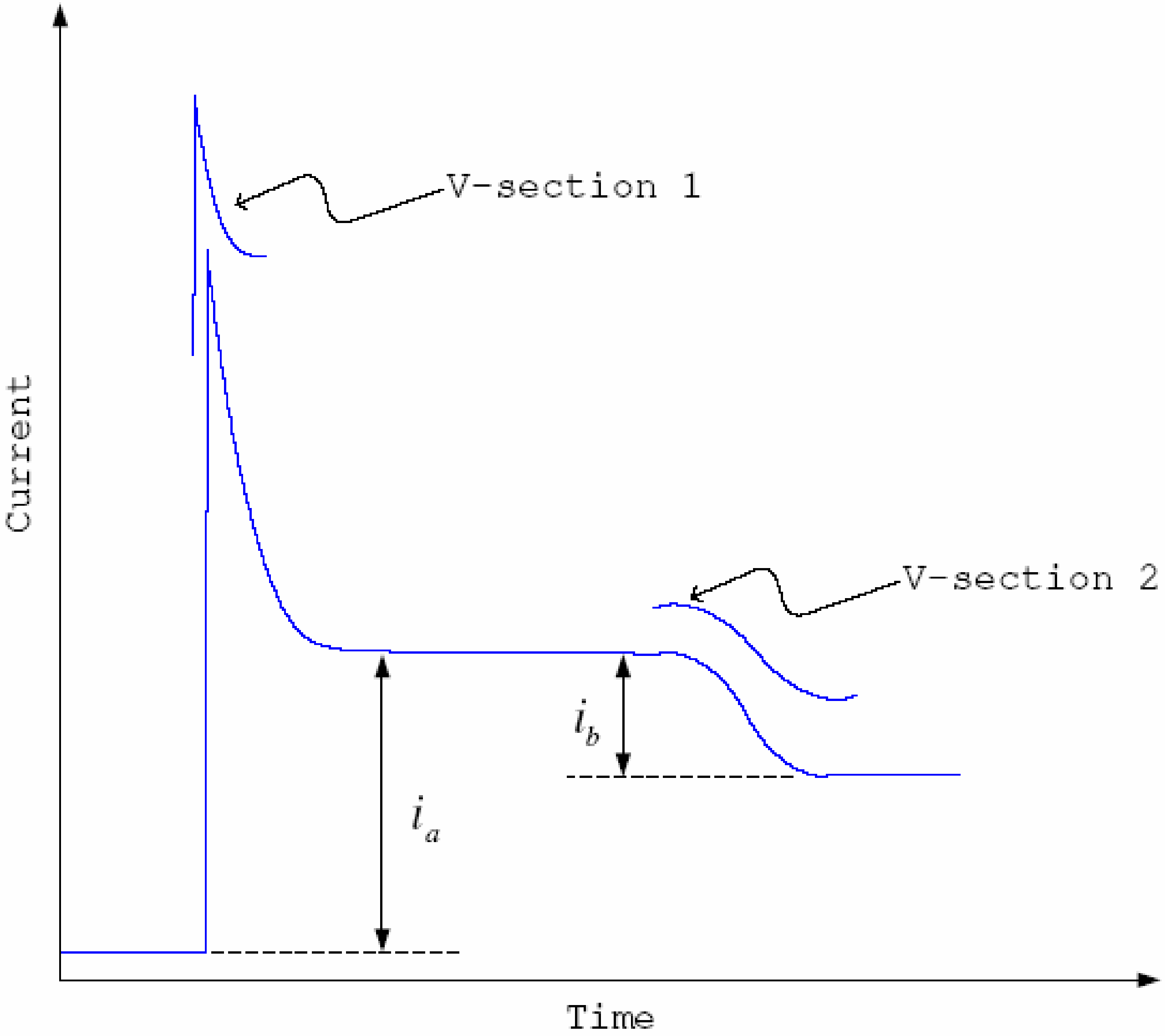
Multi-source Control Objective



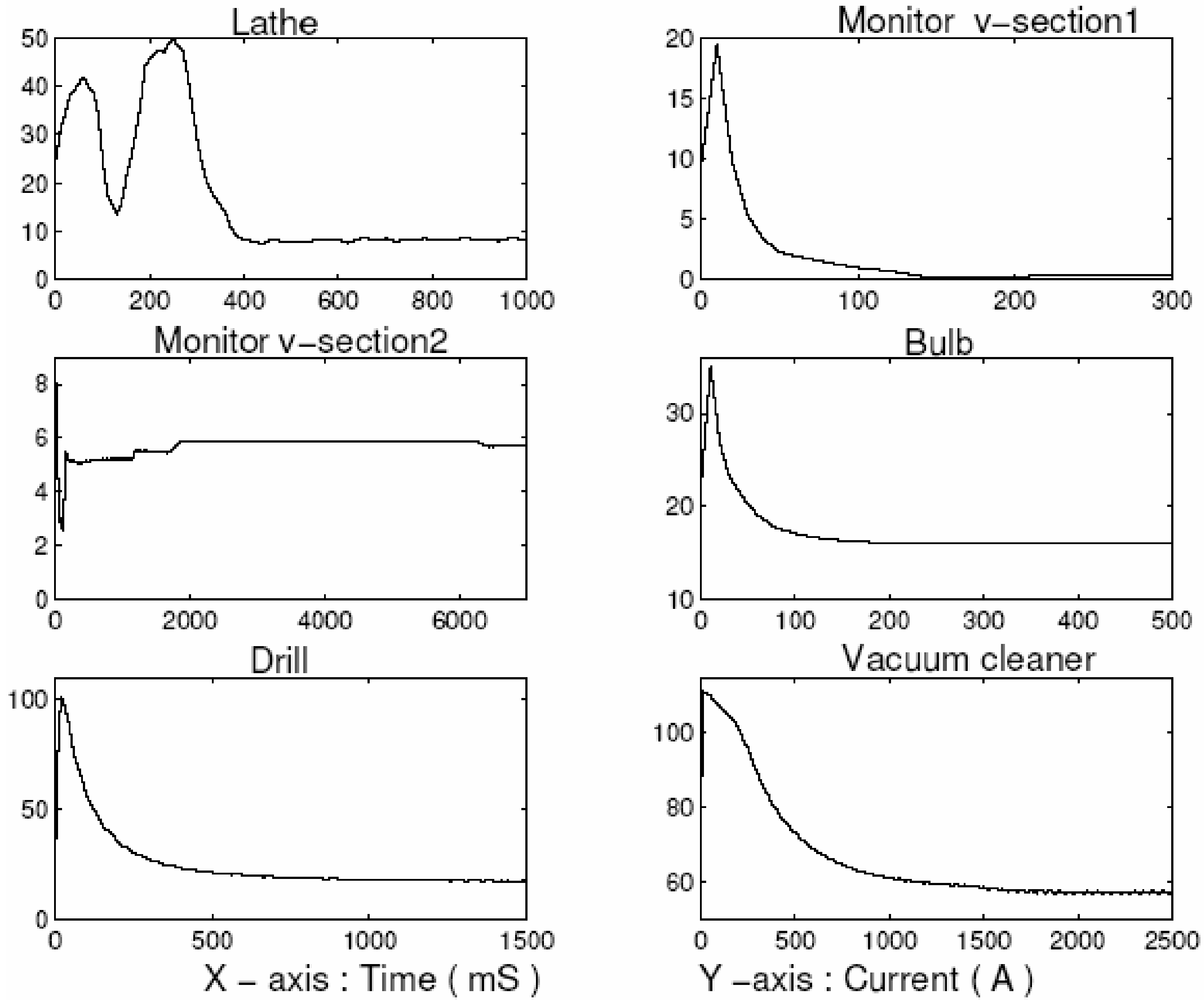
Cluster Weighted Model Concept



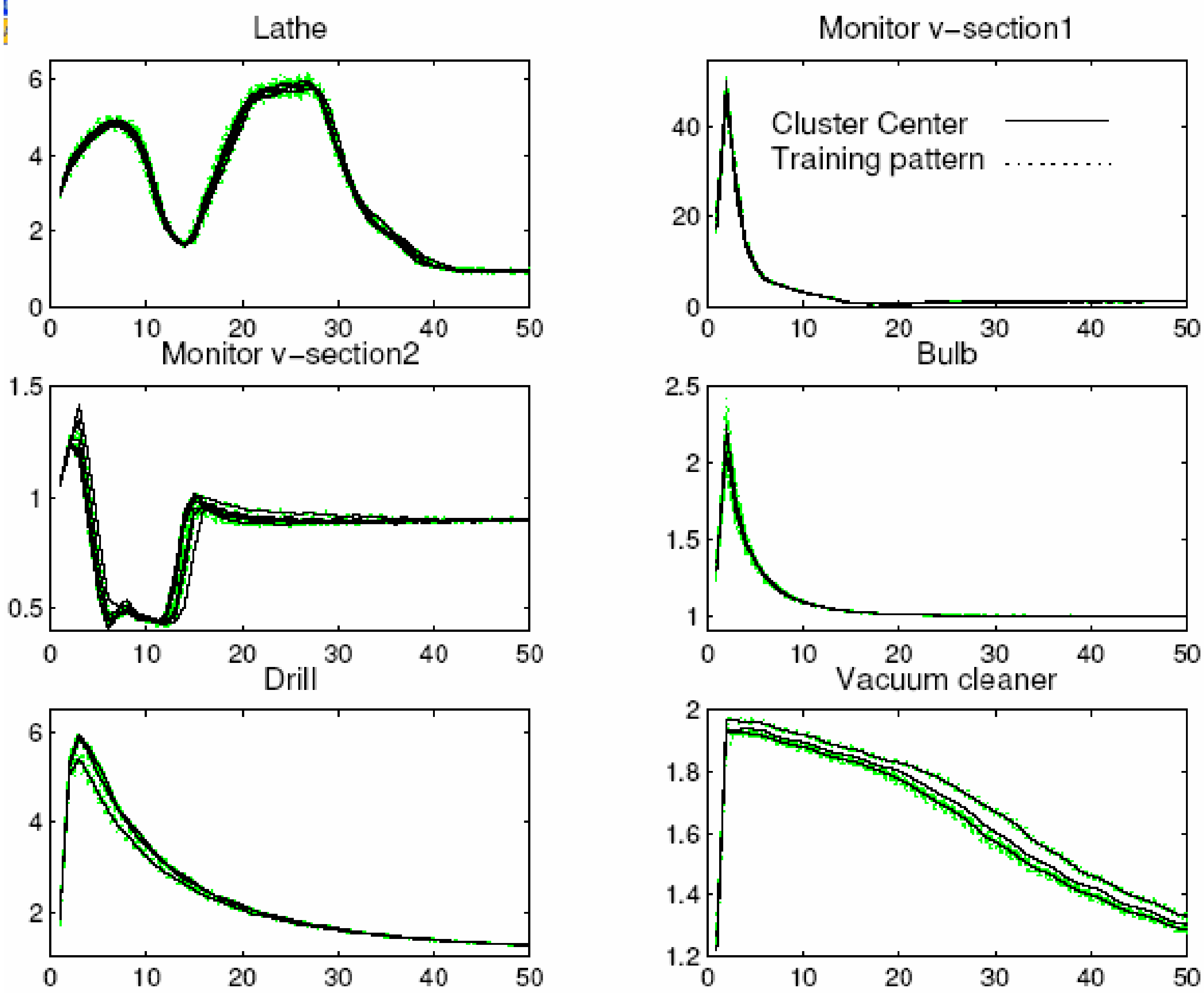
V-Section Composition



Example Transients

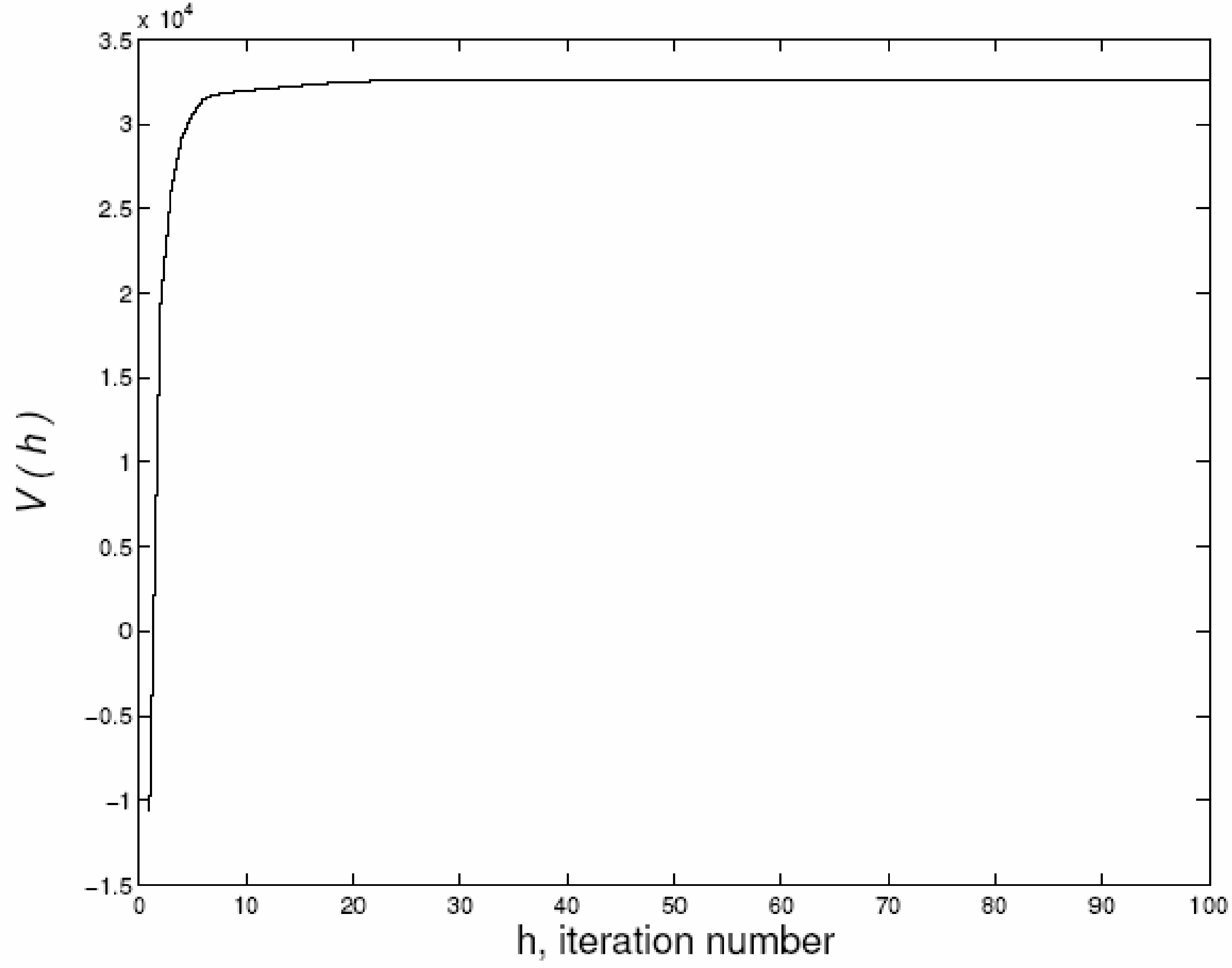


Cluster Training

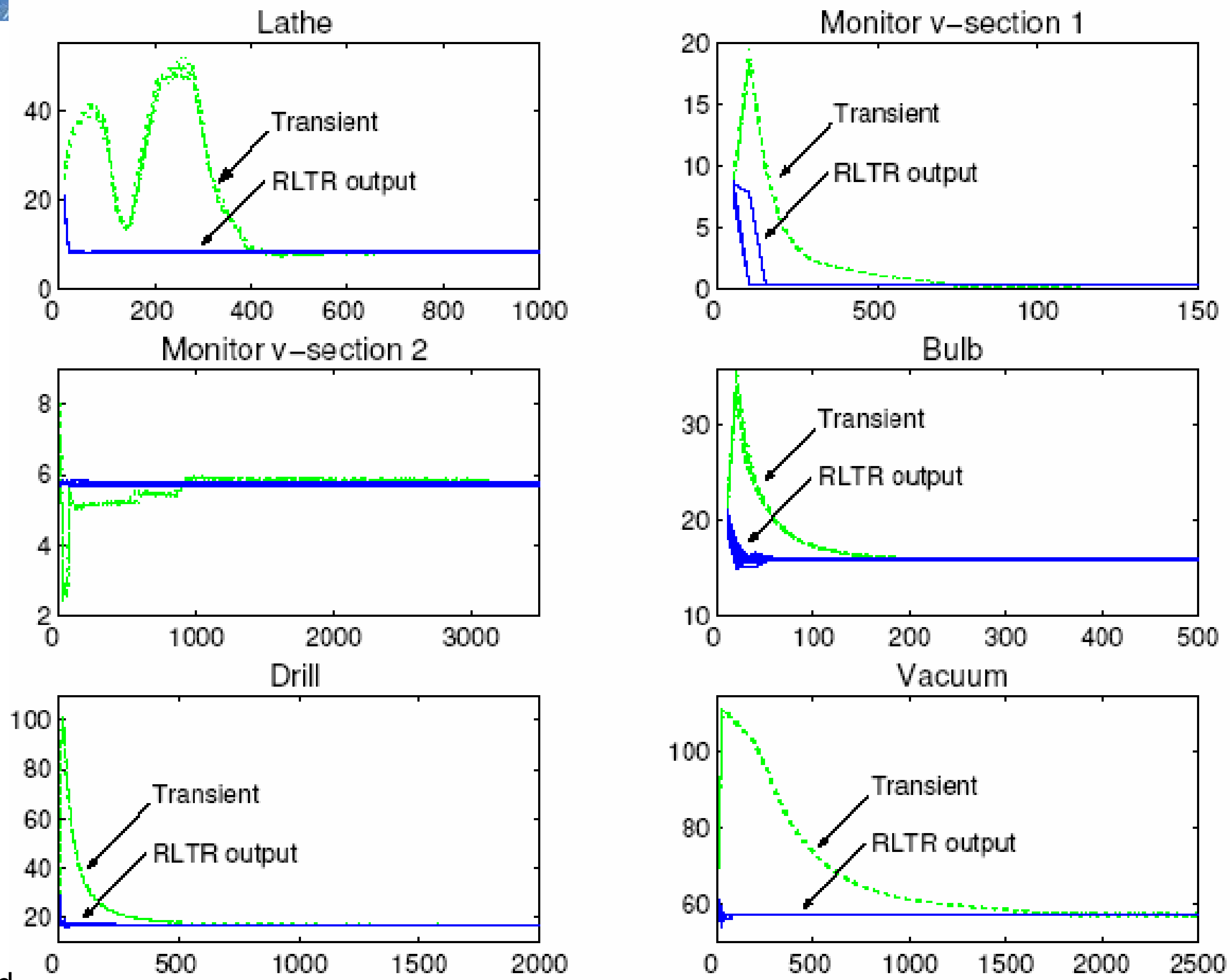


X – axis : Pattern point Y – axis : Magnitude (Normalized)

Time Evolution of Log-Likelihood

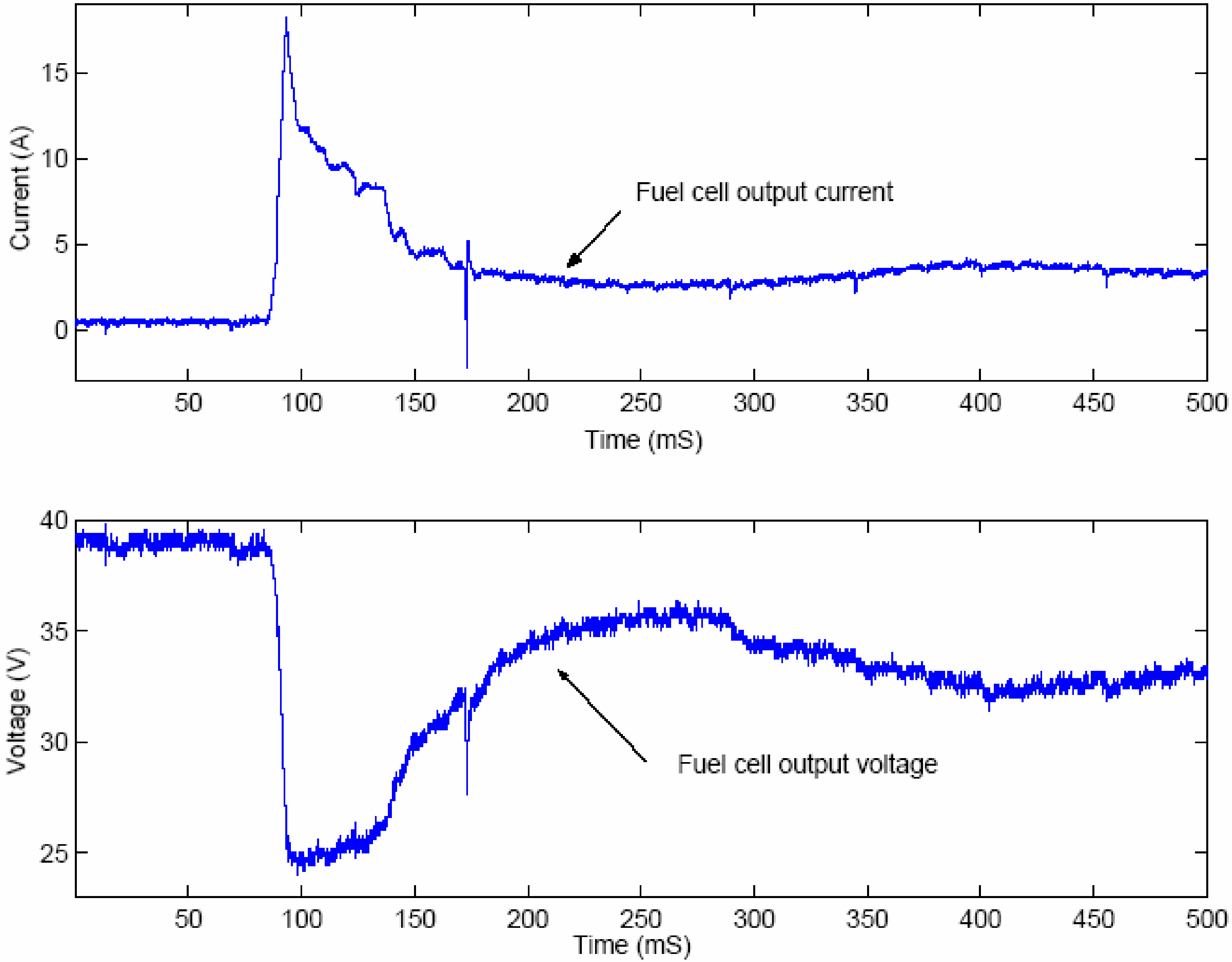


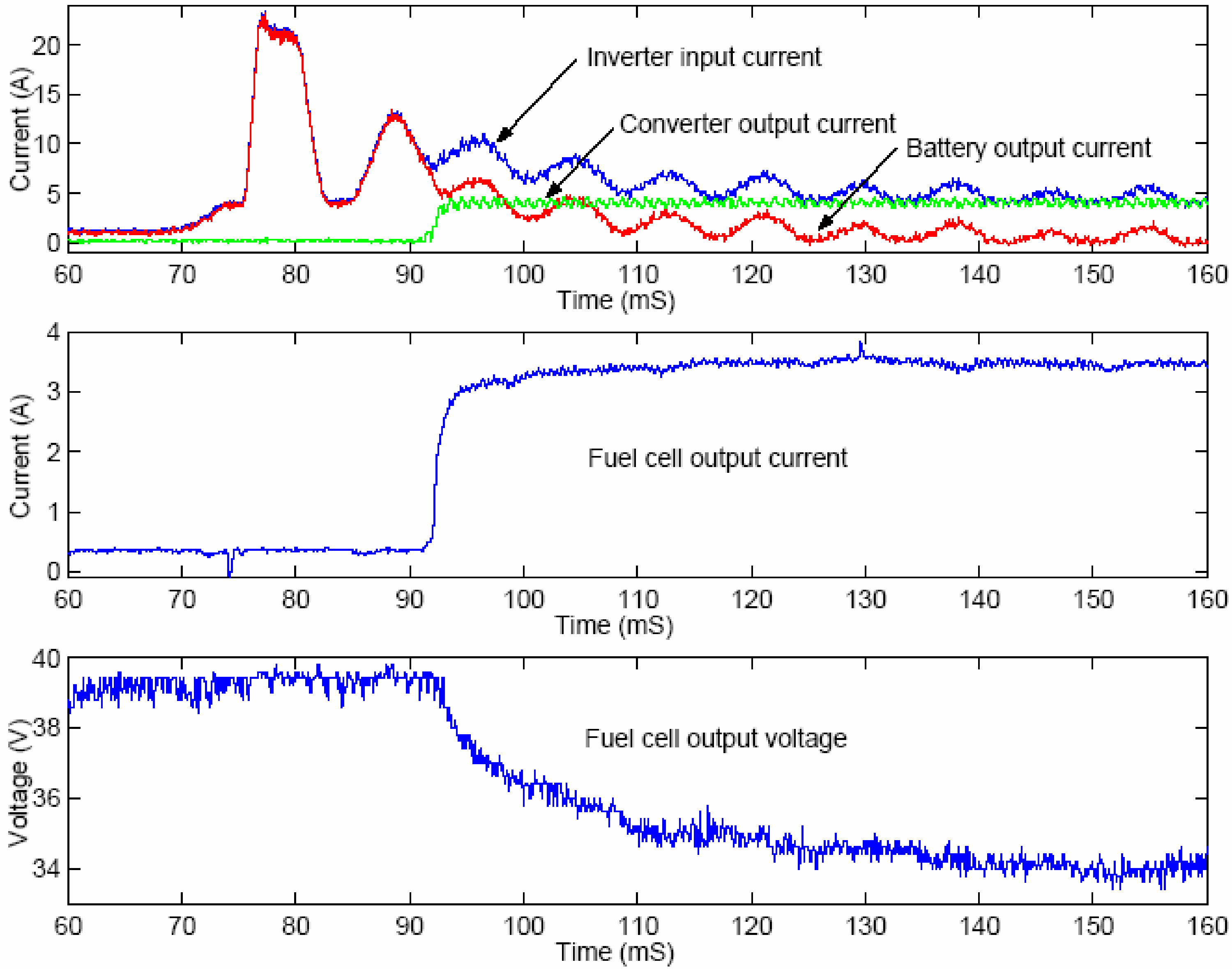
Results

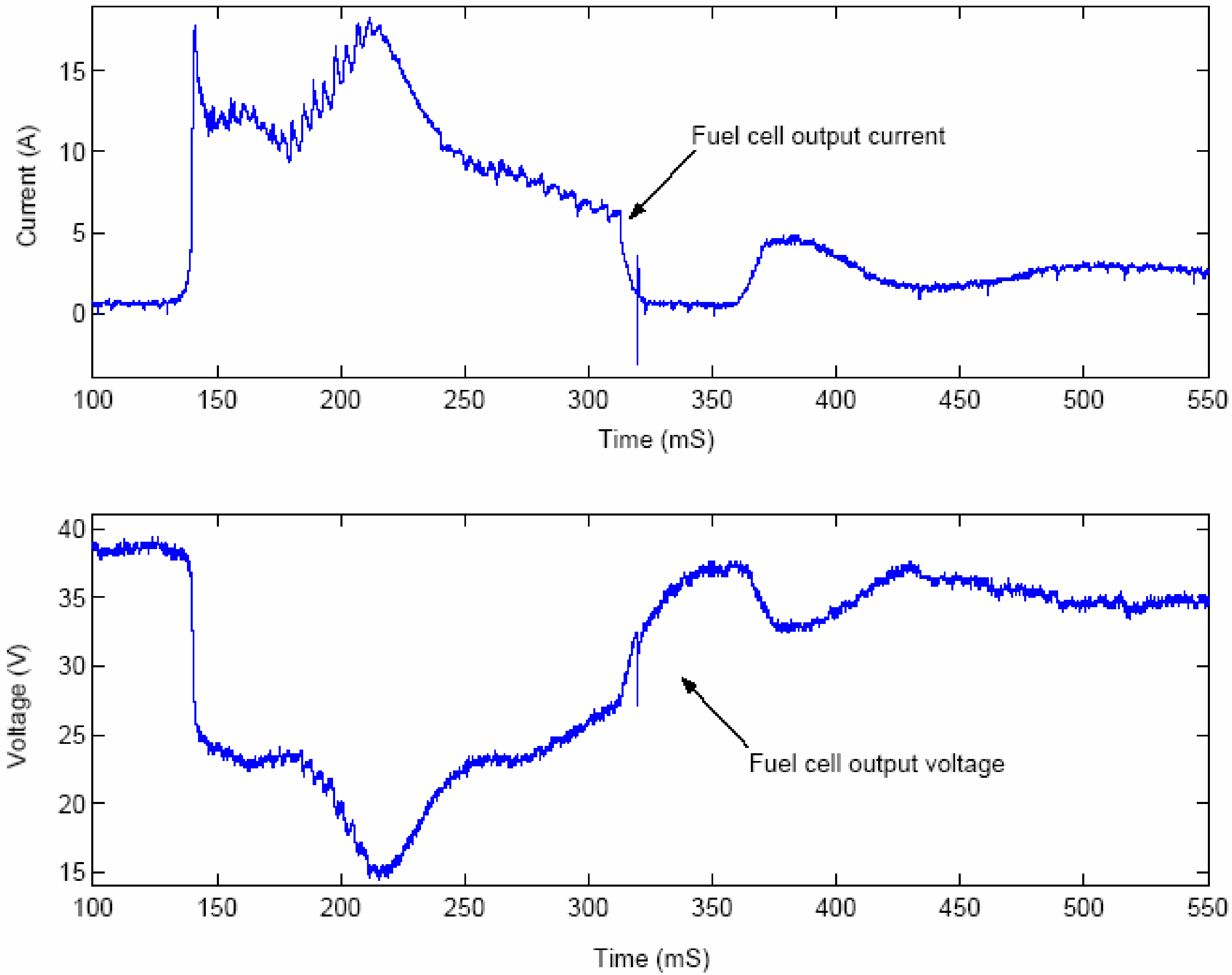


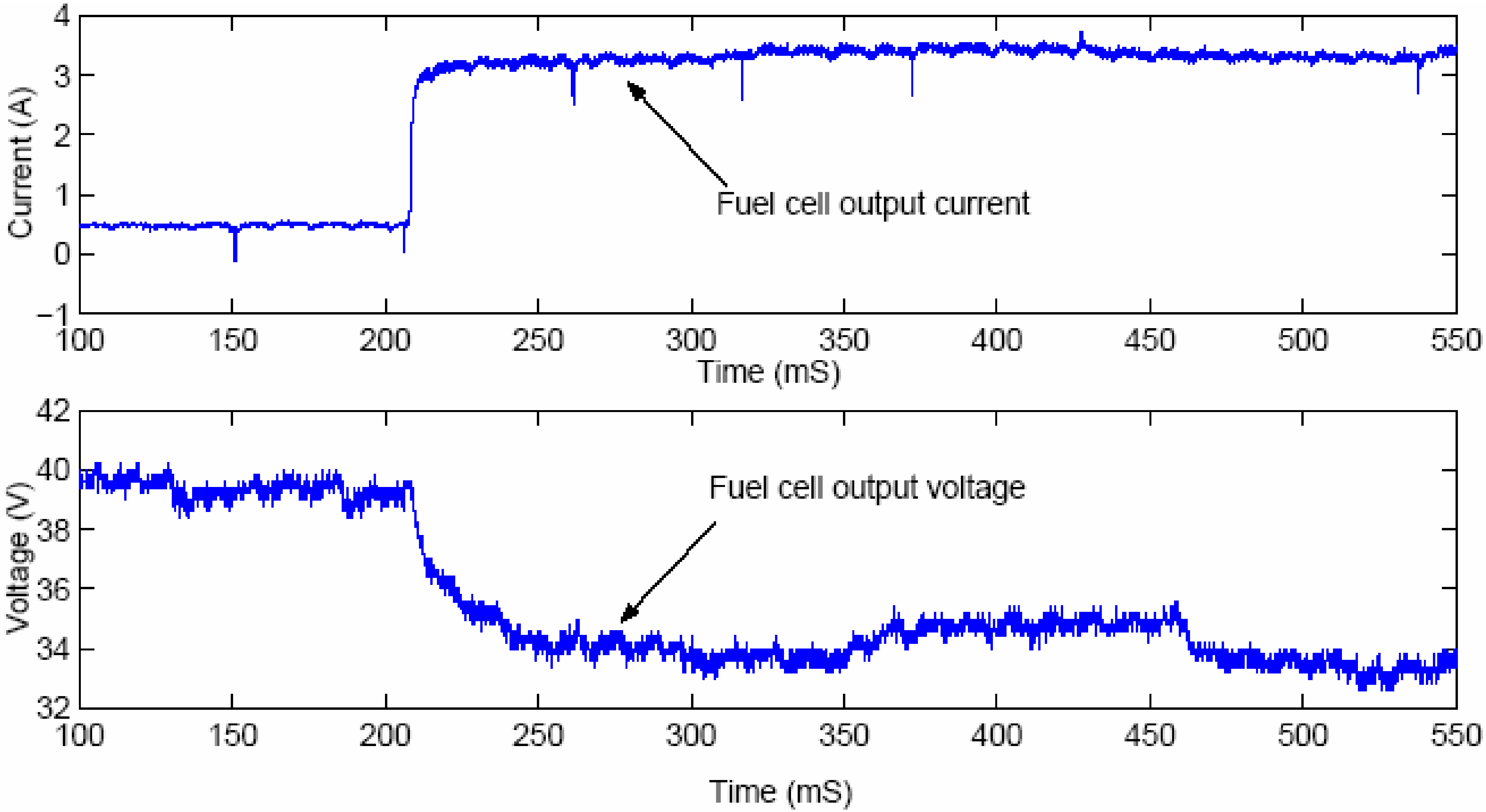
X – axis : Time (mS)   Y – axis : Current (A)

Recursive Load Transient Recognition


Fuel cell output current
Current (A)
Time (mS)
Fuel cell output voltage
Voltage (V)
Time (mS)

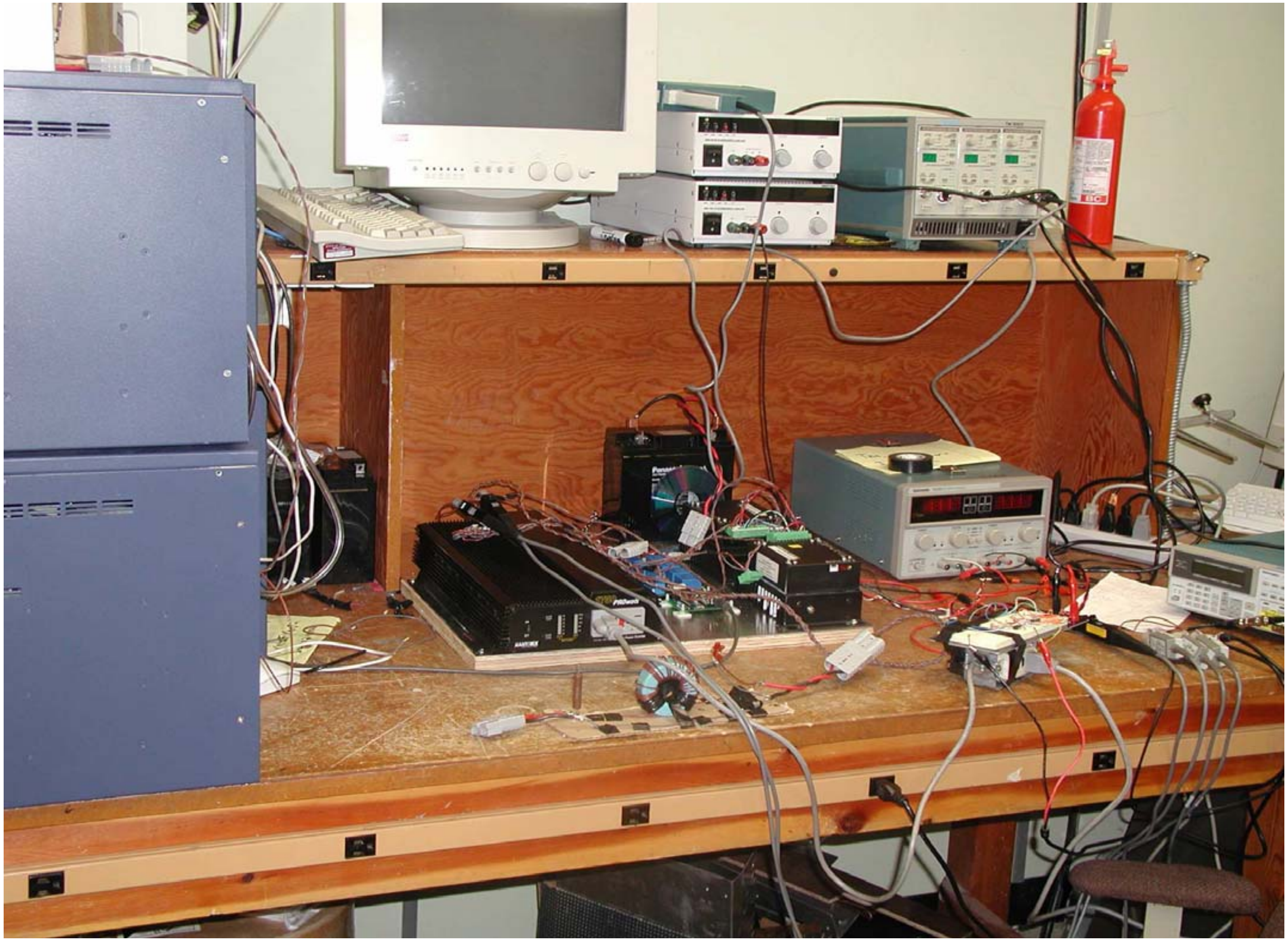

Inverter input current
Converter output current
Battery output current
Current (A)
Time (mS)
Fuel cell output current
Current (A)
Time (mS)
Fuel cell output voltage
Voltage (V)
Time (mS)


Fuel cell output current
Current (A)
15
10
5
0
100
150
200
250
300
350
400
450
500
550
Time (mS)
Fuel cell output voltage
Voltage (V)
40
35
30
25
20
15
100
150
200
250
300
350
400
450
500
550
Time (mS)



Current (A)
4
3
2
1
0
−1
100
150
200
250
300
350
400
450
500
550
Time (mS)
Fuel cell output current
Voltage (V)
42
40
38
36
34
32
100
150
200
250
300
350
400
450
500
550
Time (mS)
Fuel cell output voltage

Multisource Implementation



Multisource Implementation Status

- RCWM theory developed
- Control works in simulations
- Hardware is built, works with AWG
- FPGA real-time platform identified
- Need to code RCWM in FPGA
- Patent application is submitted

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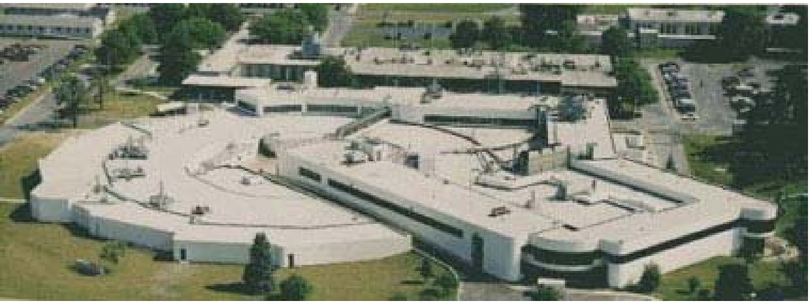
MSU Materials X-ray Characterization Facility at the National Synchrotron Light Source

nsls IR UV X



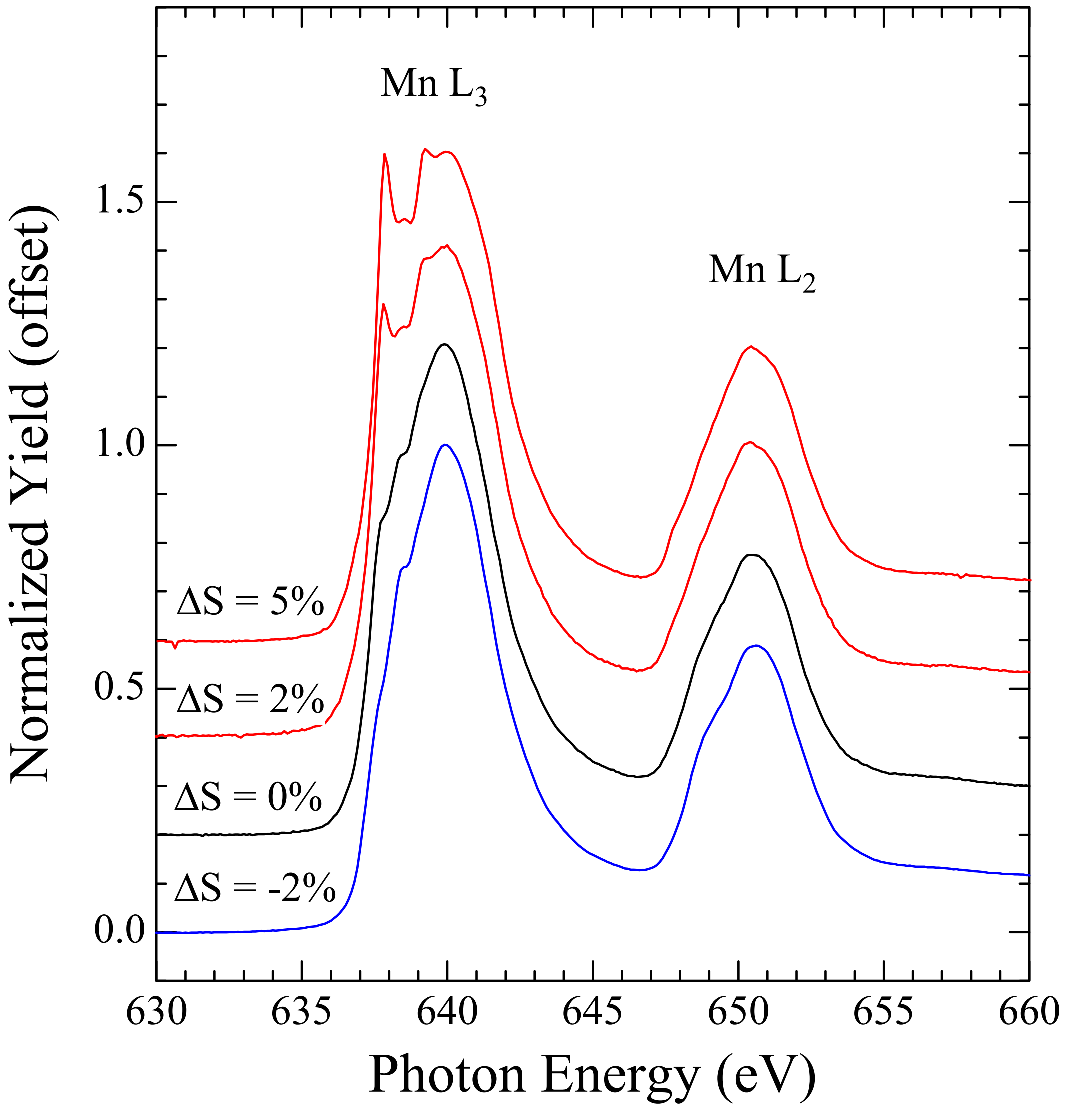
U4B - Soft X-rays

X23 - Hard X-rays - NEW

Using synchrotrons to understand material properties.

- **XAS**
- **XAFS**
- **XRS**
- **Characterization of buried interfaces at angstrom resolution**

Interface Stress (LCMO)

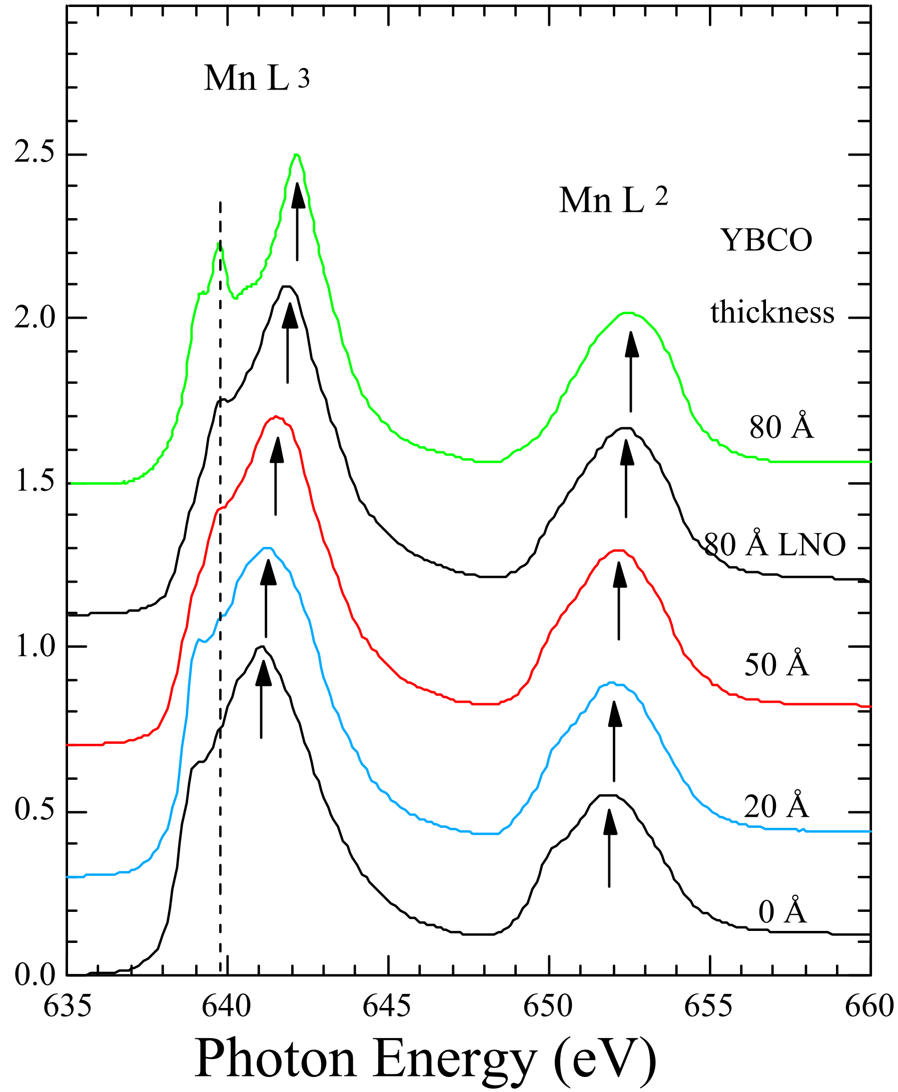


Variation in chemical signature of solid oxide fuel cell material ($La_xCa_{1-x}MnO_3$) with interfacial stress ΔS.

Stress created by selecting **substrate** to create a lattice mismatch.

Submitted: Phys. Rev. B (03)

Interface Stress (LSMO)



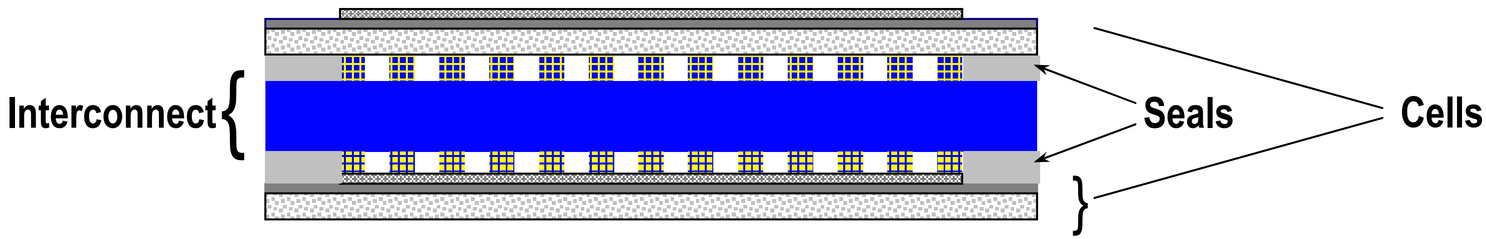
Variation in chemical signature of solid oxide fuel cell material ($La_xSr_{1-x}MnO_3$) with overlayer stress.

Stress created by **changing thickness of an overlayer** with a lattice mismatch.

REF: Appl. Phys. Lett. 75, 3384 (02)

SOFC Stack Current Collector

Function and Problems



- **Acts as a physical barrier between the fuel and oxidant (hermetic, chemically and mechanically stable, and thermally shock resistant)**
- **Acts as a low resistivity electrical conduit over the lifetime of the device**
- **Provides mechanical support and stability to the stack**
- ***"…it appears that in the long term, few if any commercially available heat-resistant alloys will completely satisfy the tecchnical requirements as the interconnect components in SOFC stacks."* Z. Yang, et al. JES 150, A1188 (2003)**
- **Design new bulk alloys, e.g. Crofer 22 APU**
- **Surface engineering: surface alloy or surface coatings**
  - **New problems: Adhesion, interdiffusion, wear resistance, etc.**

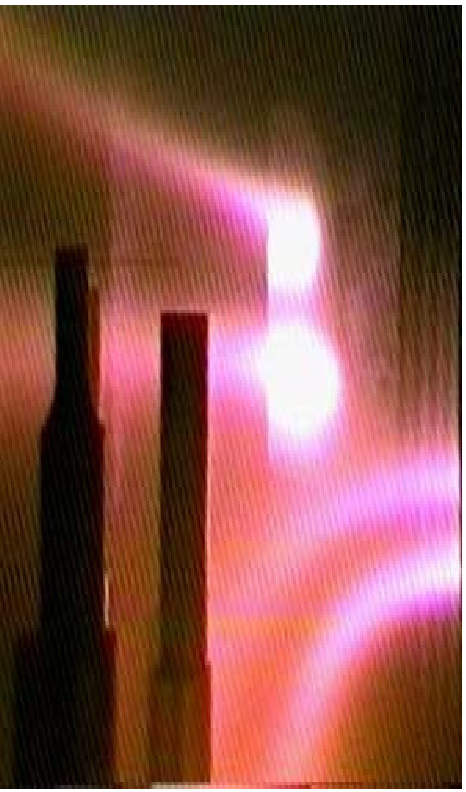
*** Jeff Stevenson - PNNL**

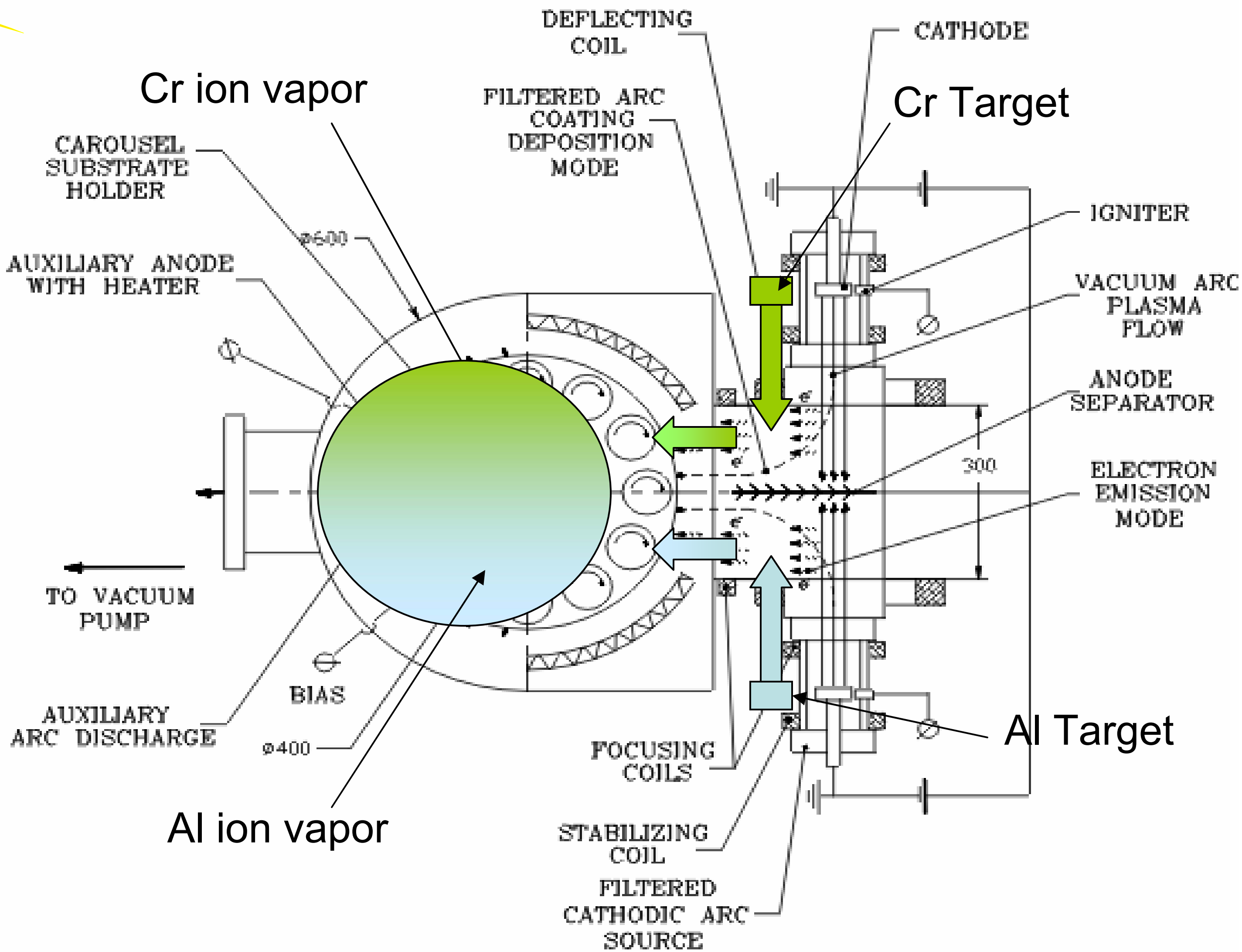
CrAlN multilayer coatings

- Polished (1500 grit) steel disks: 304, 440, Crofer APU 22
- Multilayer coating at Arcomac: $\{(CrN)_m/(CrN)_n(AlN)_n\}_p$
  Wear resistant; CrN to maintain conductivity; AlN for oxidation resistance
- Anneal in air furnace at 800 ^{o}C for 1-25 hours
- Analysis: RBS, NRA, SEM, AFM, TEM, XPS, ASR

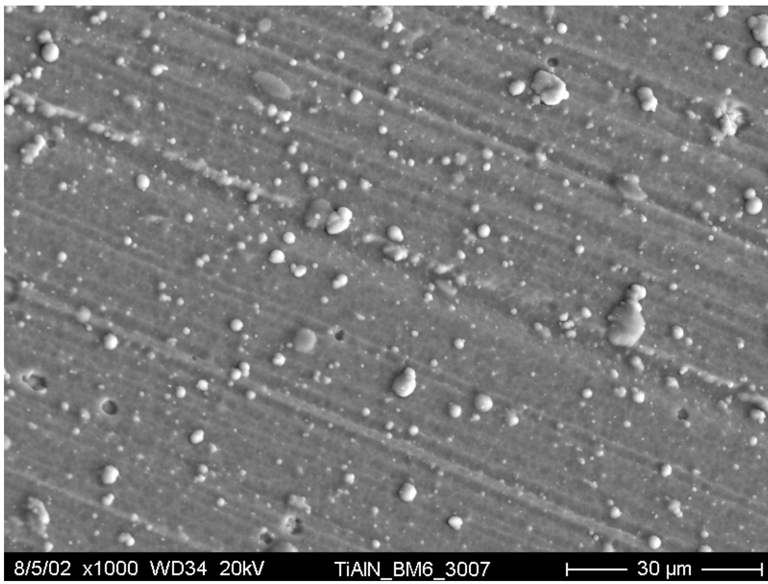
- **Goal: Tailor the multilayer structure and composition to optimize oxidation resistance, conductivity, adhesion**

Large Area Filtered Arc Deposition (LAFAD) Technology





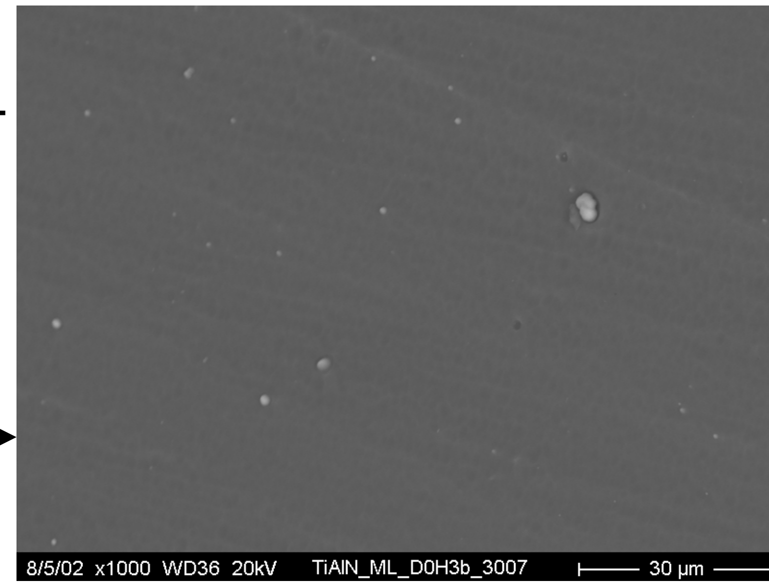
Benefits of Filtered Arc Deposition



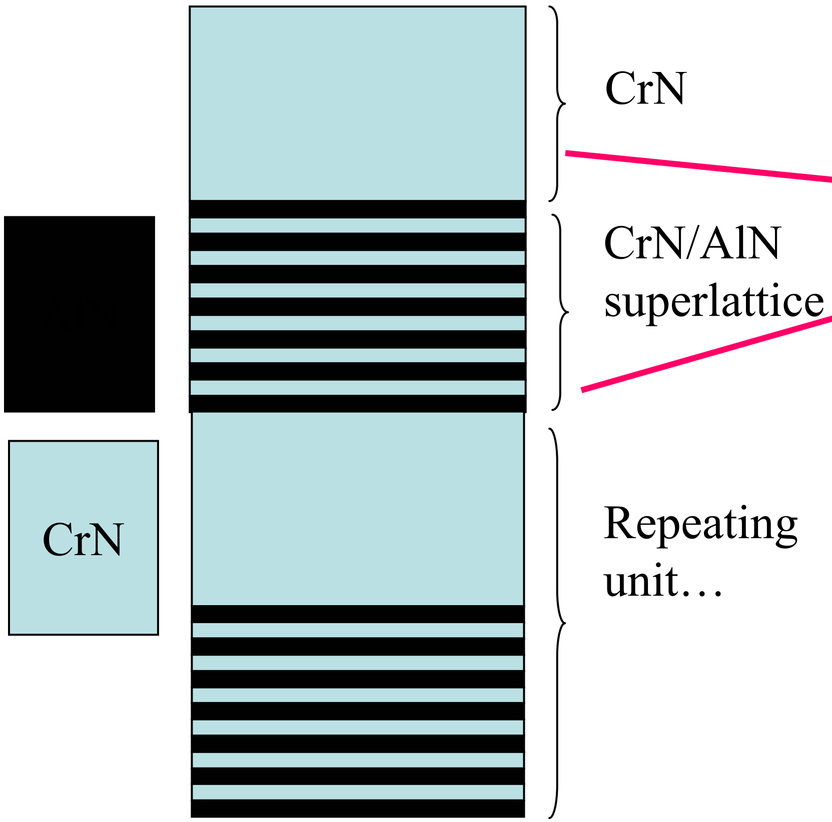
TiAlN

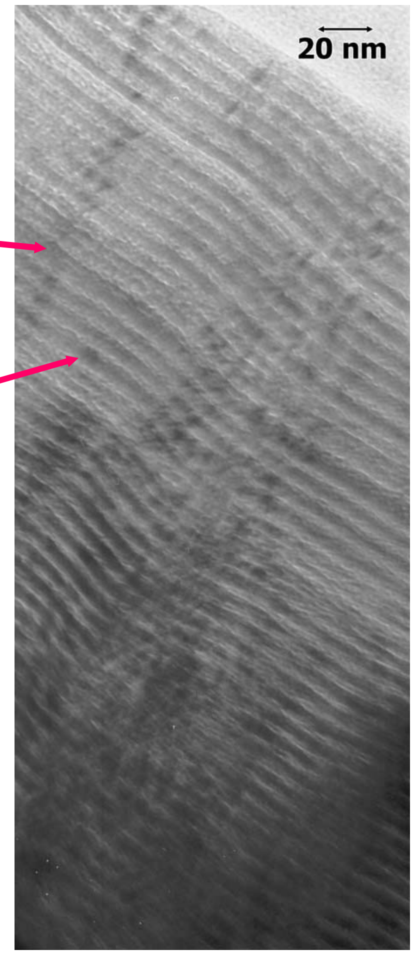
CONVENTIONAL (KENNAMETAL)

ARCOMAC™



Structure of multilayer coatings





TEM of coating (D. Gelles)

Multilayer coatings on steel (low cost)

AlN for oxidation resistance

CrN for electrical conductivity

Conduction mechanism – tunneling

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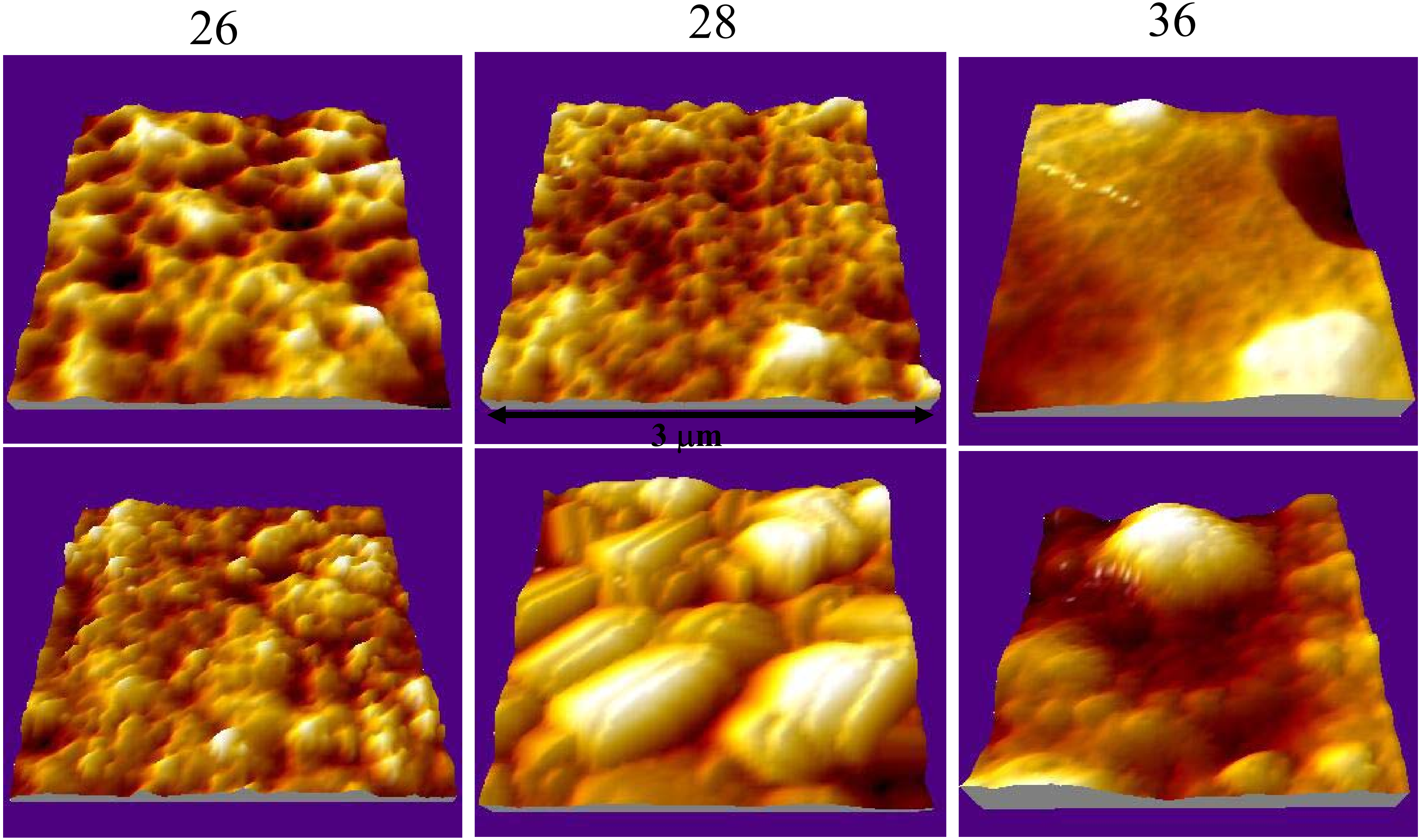
Architecture of coatings

$$\{(CrN)_m/(CrN/AlN)_n\}_p$$

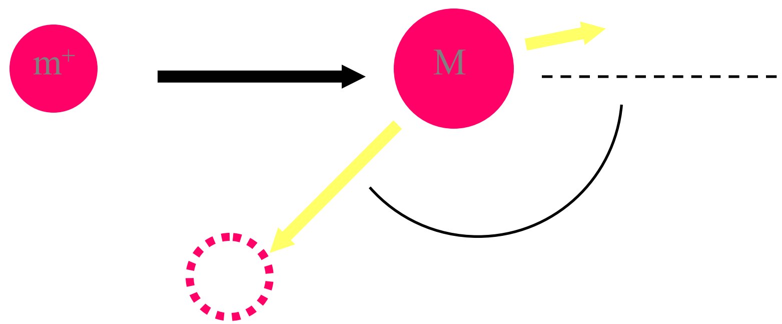
Sample	m(s)	n(s)	p(reps)	Description
010	120	60	20	60m DR
018	105	15	15	30m DR
021	40	20	30	30m DR
026	40	20	60	60m SR
028	40	20	60	60m DR
036	--	4hrs	--	superlattice
023	30m	--	--	thick CrN

AFM before(top)/after(bottom) oxidation: 800 ^{o}C in air for 25 hr



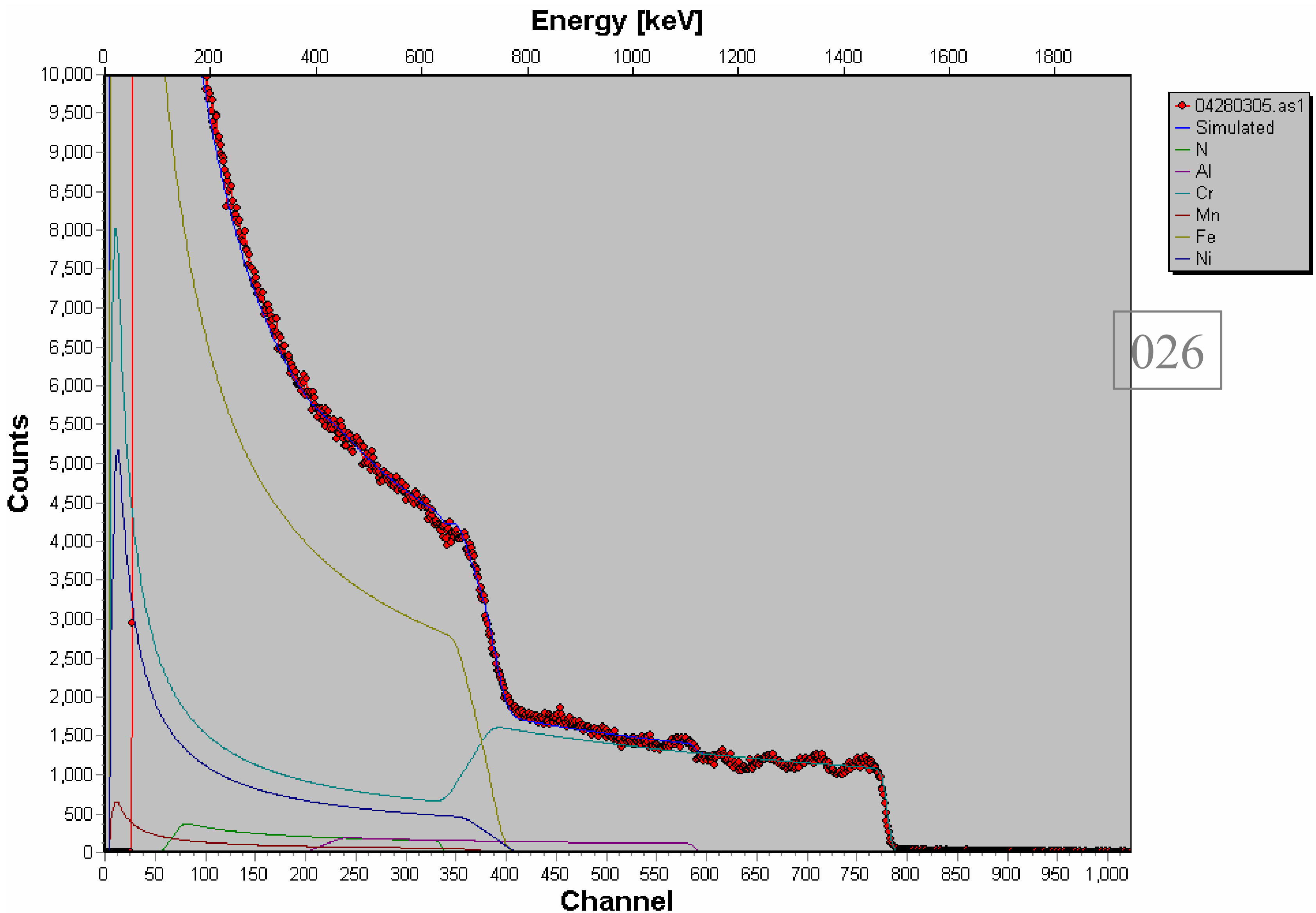
Ion Beam Analysis: RBS, NRA

- RBS: 2 MeV He^+ ions
- NRA: 1 MeV d^+ ions
- Yield = Q σ Ω (Nt)
- Quantitative



- Kinematics: mass resolution
- Energy loss: depth scale
- Cross section: RBS has more sensitivity for heavy elements
- Nuclear reaction: use (d^+,p) reactions for light elements (O, N, C)

RBS and simulation: 2 MeV He^+



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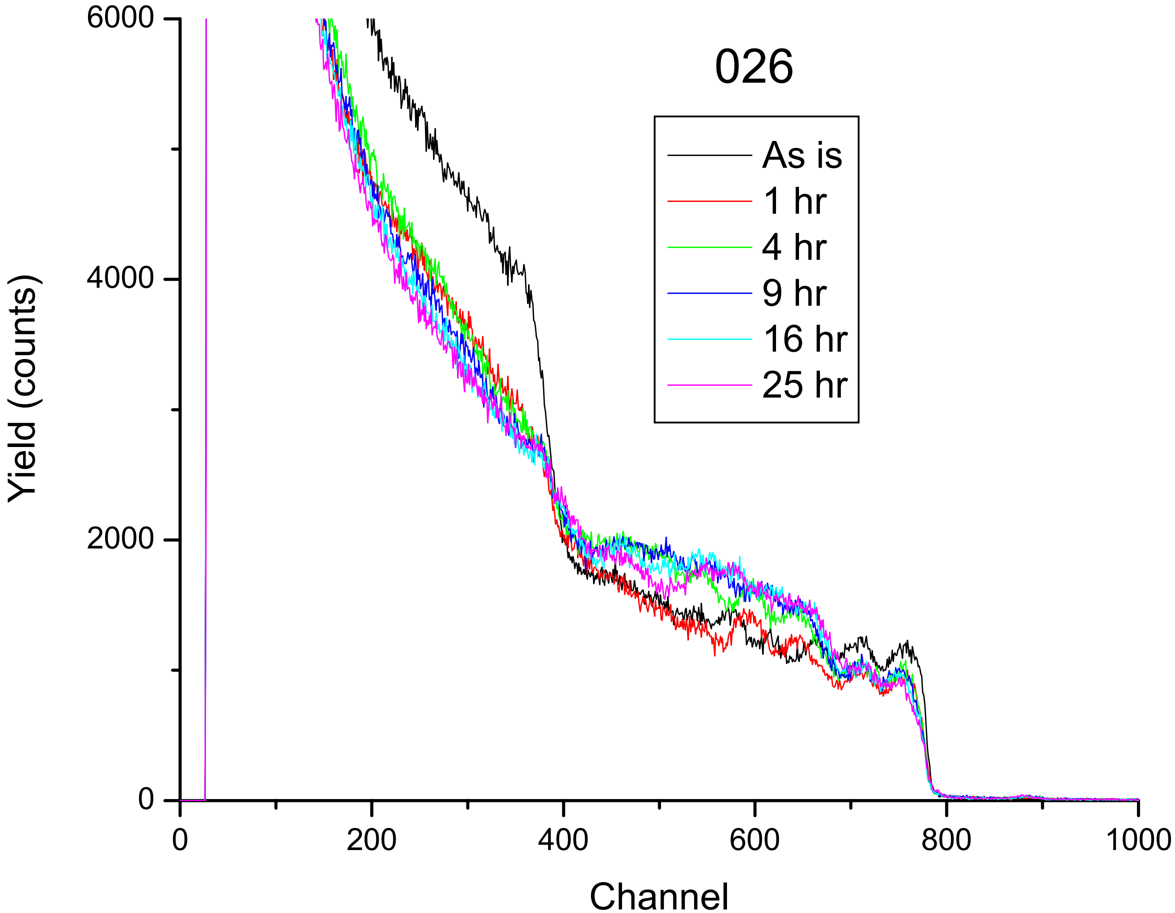
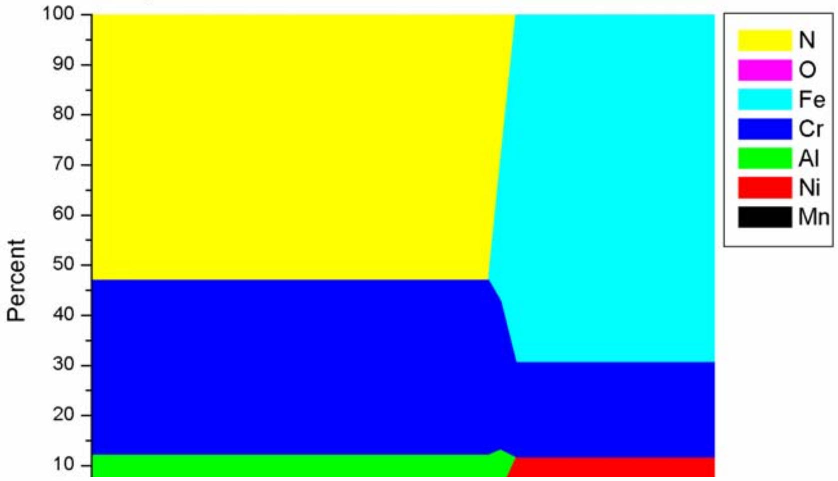
Evolution of RBS spectra with annealing



- Fit thickness, composition in each layer
- Most sensitive to the heavy elements
- Check against SiO_2 and Si_3N_4 standards

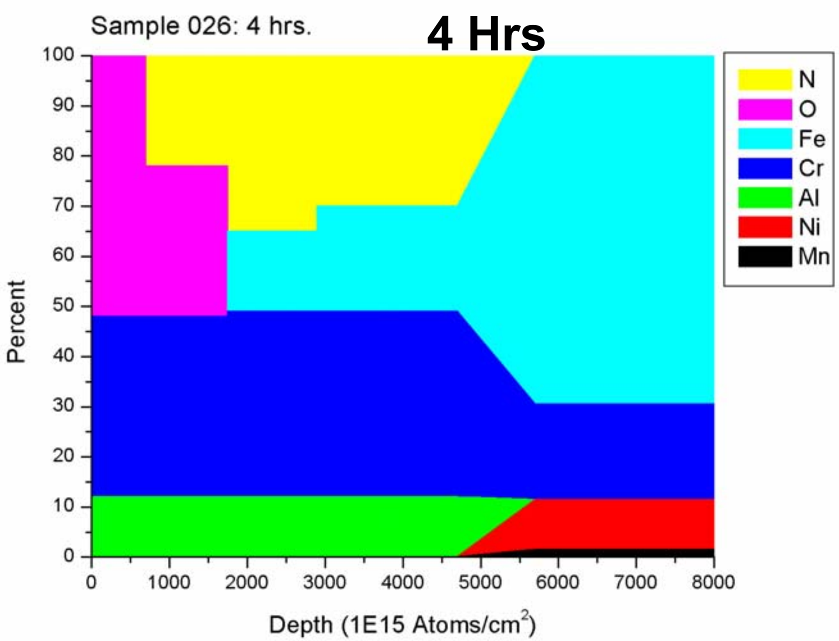
RBS Temporal Concentration Profiles: 026 @ 800 C

0 Hrs

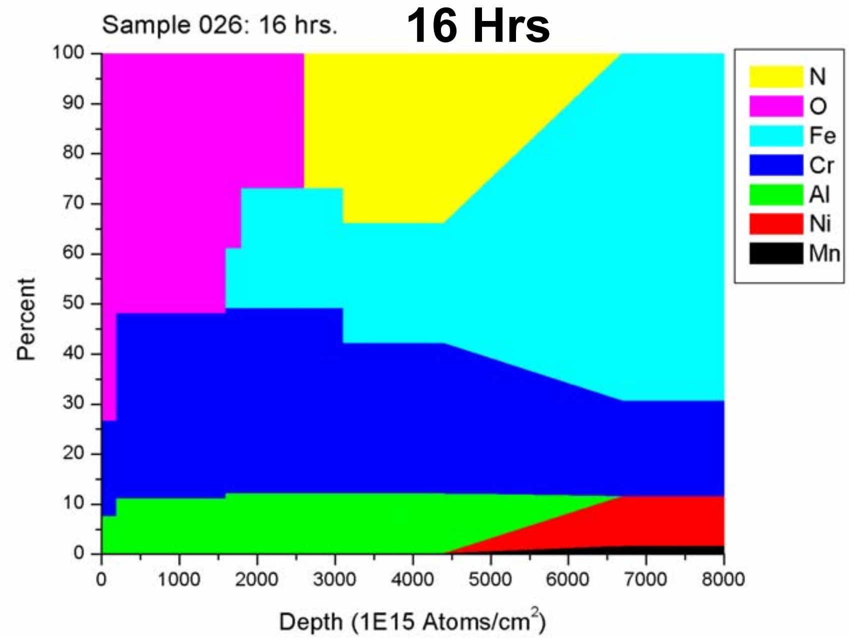


1 Hrs

4 Hrs

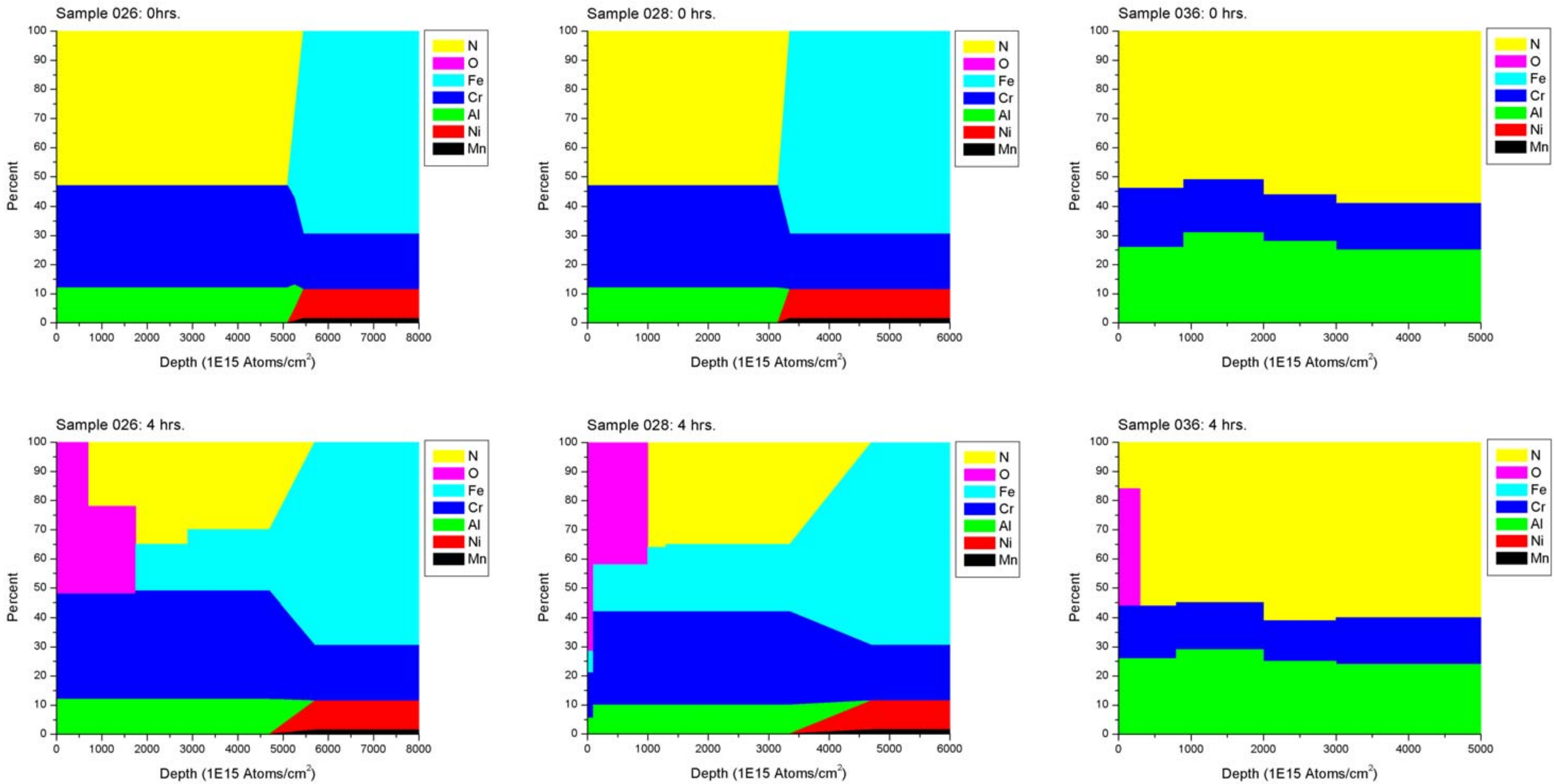


16 Hrs

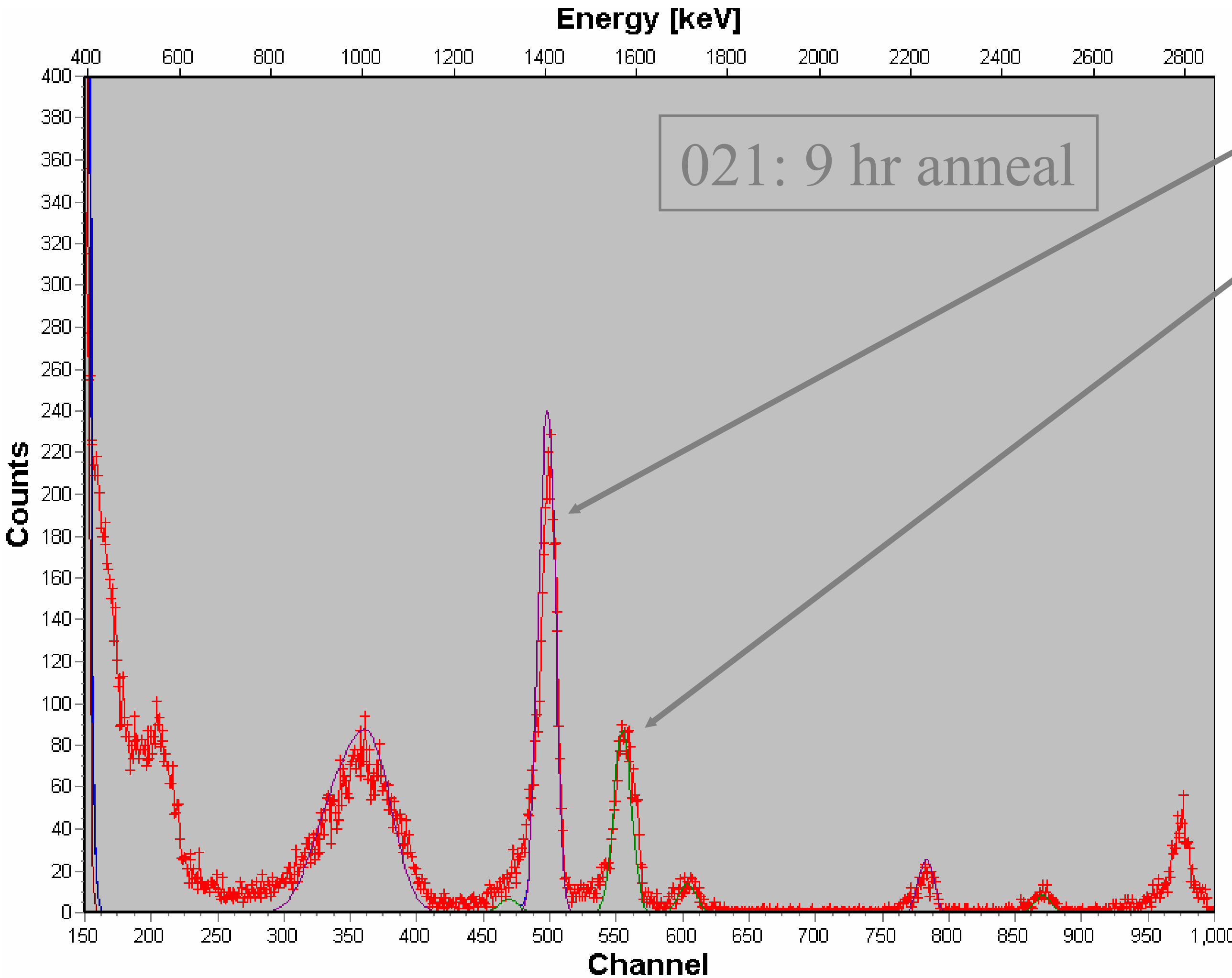


RBS Concentration Profiles:

Before(top) after (bottom) 4 hrs @ 800 C

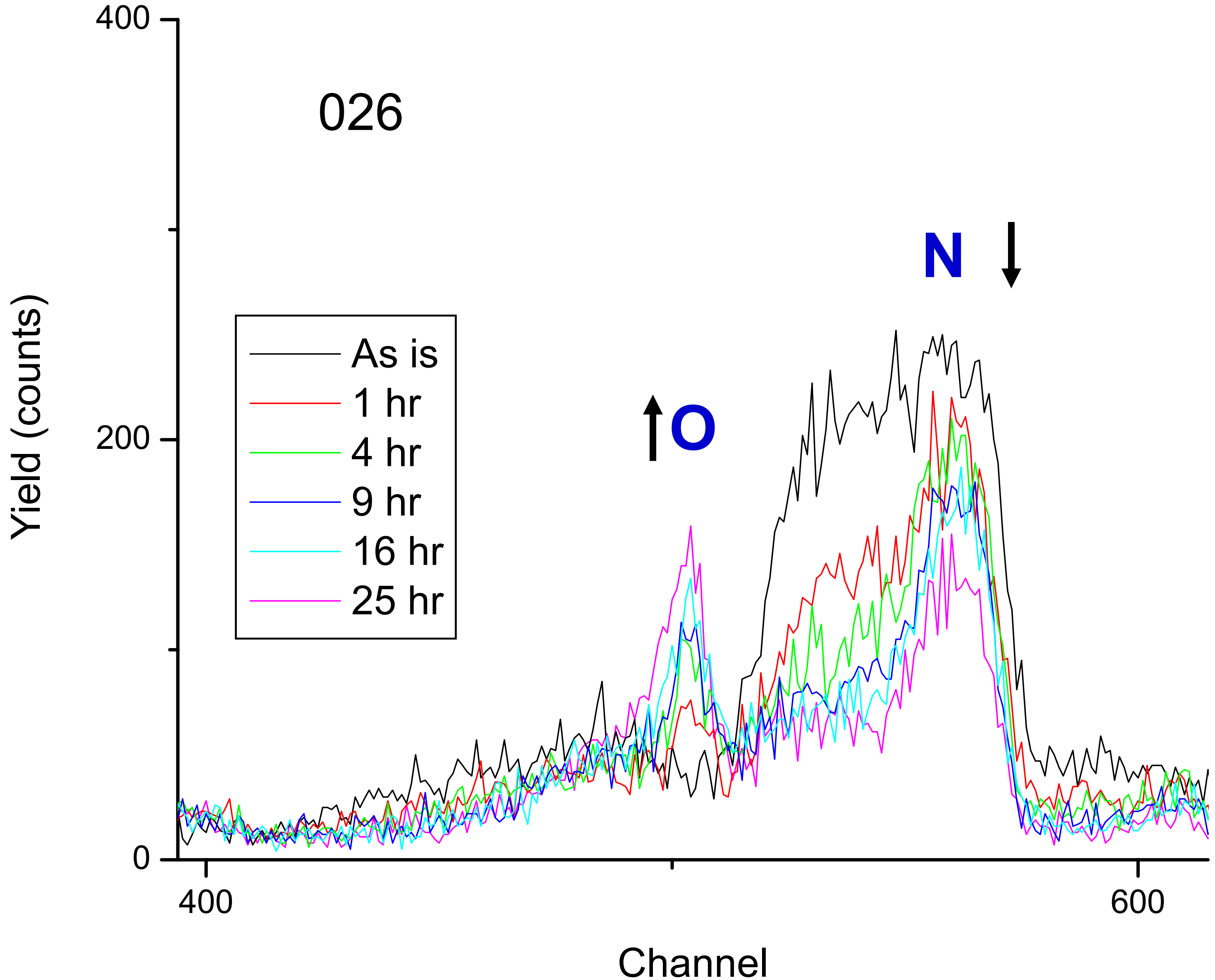


NRA and simulation: 1 MeV d^+



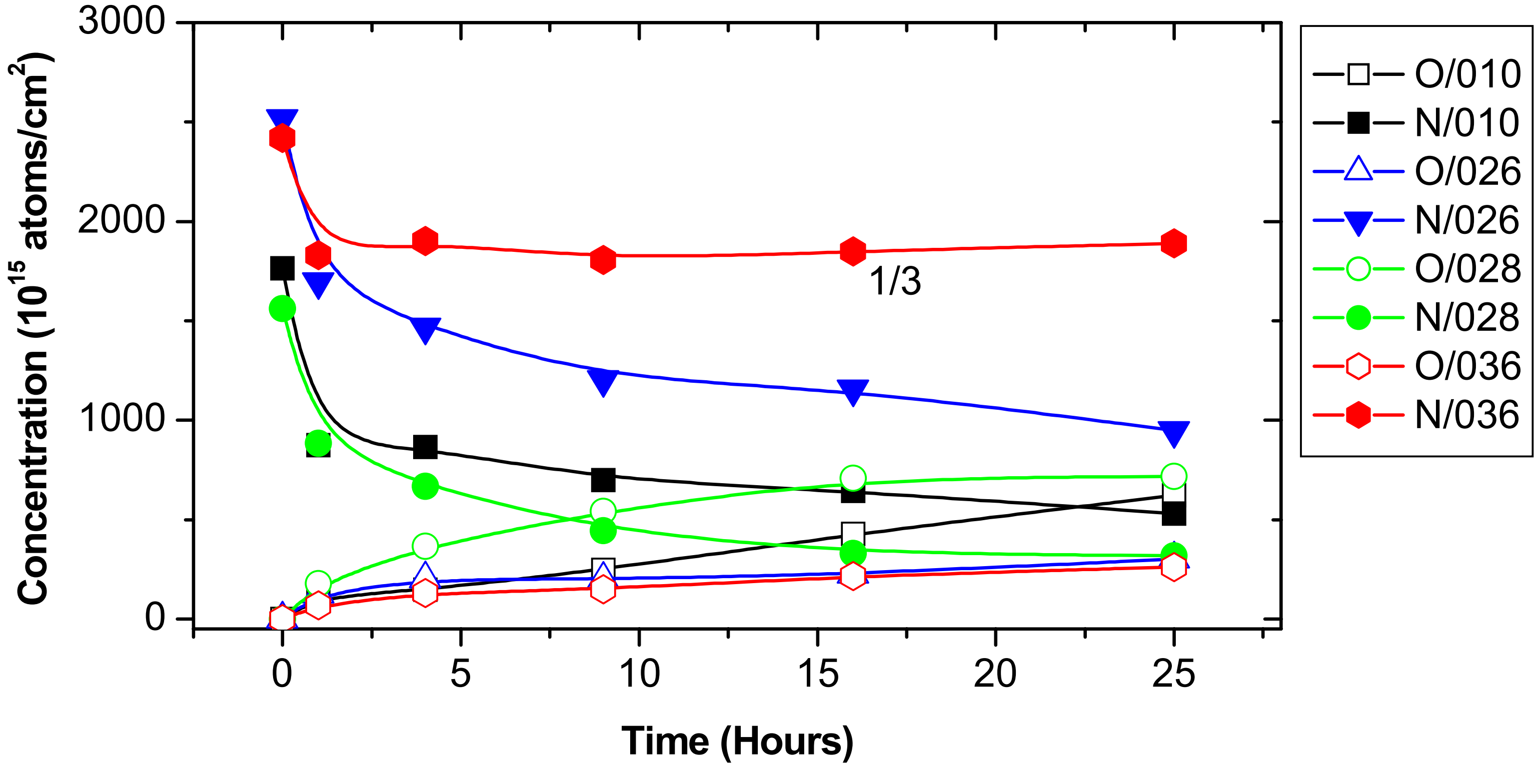
- $^{16}O(d,p)^{17}O$
  $^{14}N(d,p)^{15}N$
- Fit thickness, composition in coating
- Match total conc. in RBS
- Use SiO_2 and Si_3N_4 standards

Test of Oxidation
Evolution of N and O peaks with annealing

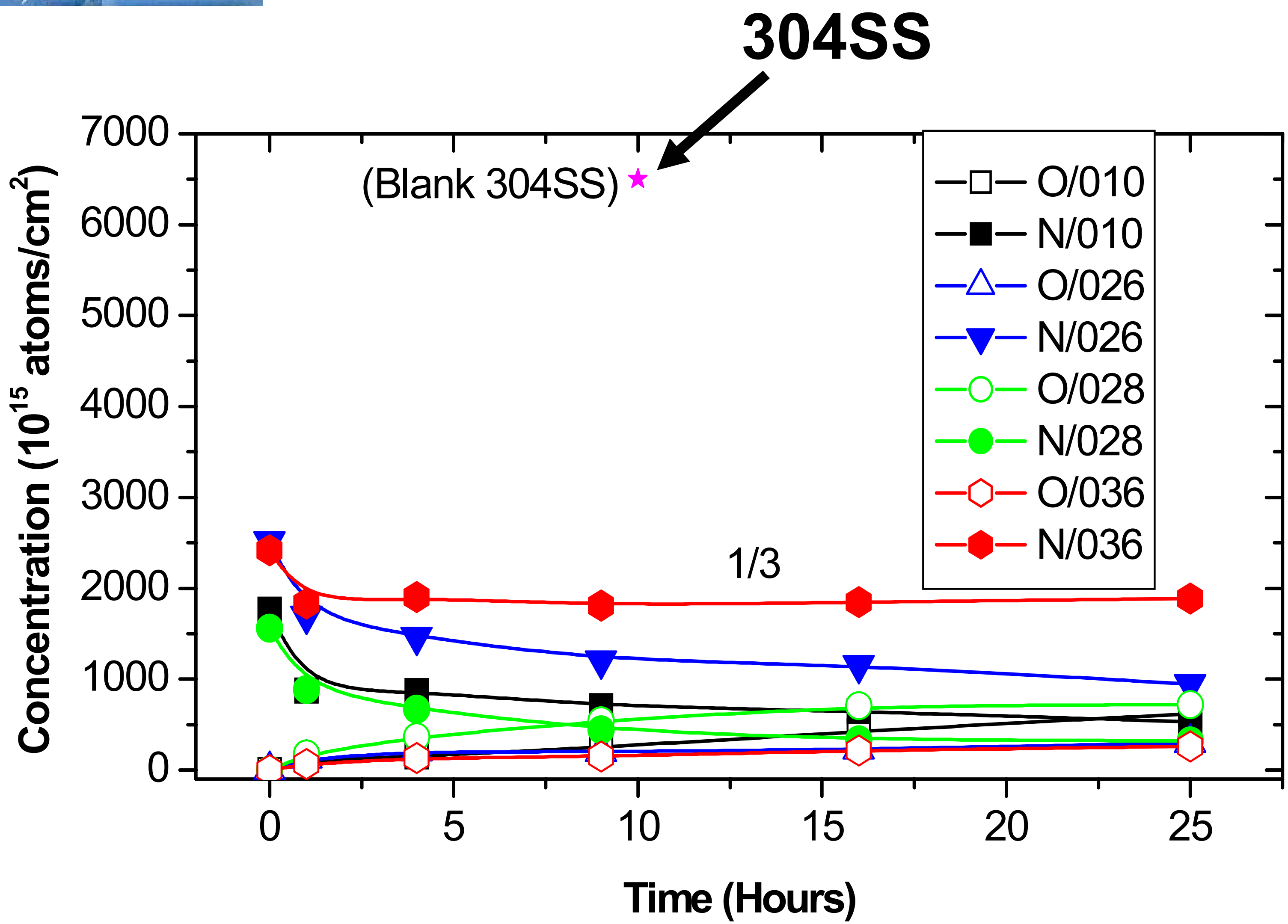


Test of Oxidation

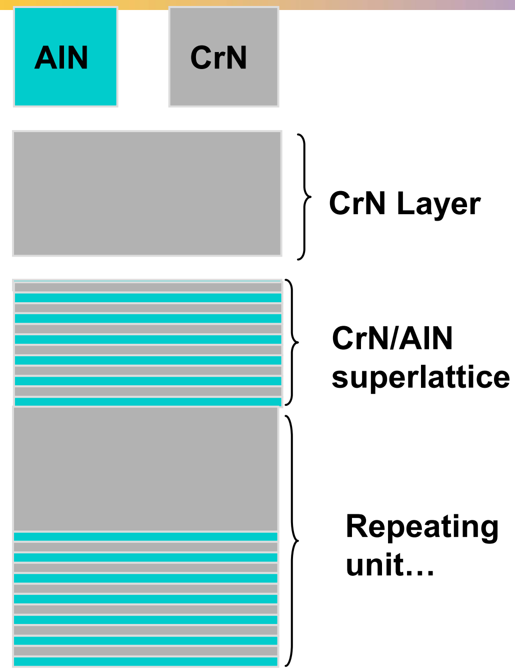
Total Nitrogen and Oxygen Content: Evolution with annealing time @ 800 °C

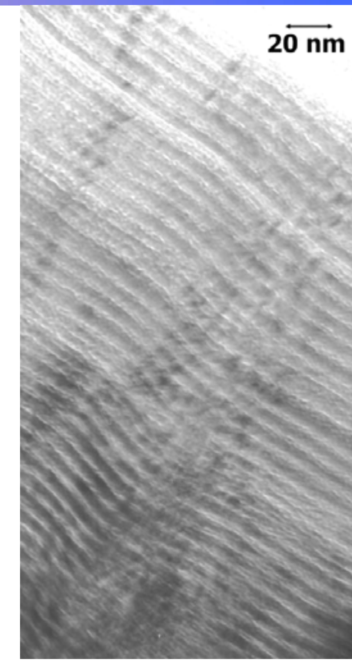


Comparison with uncoated Blank



ASR Results for Coated Crofer 22APU

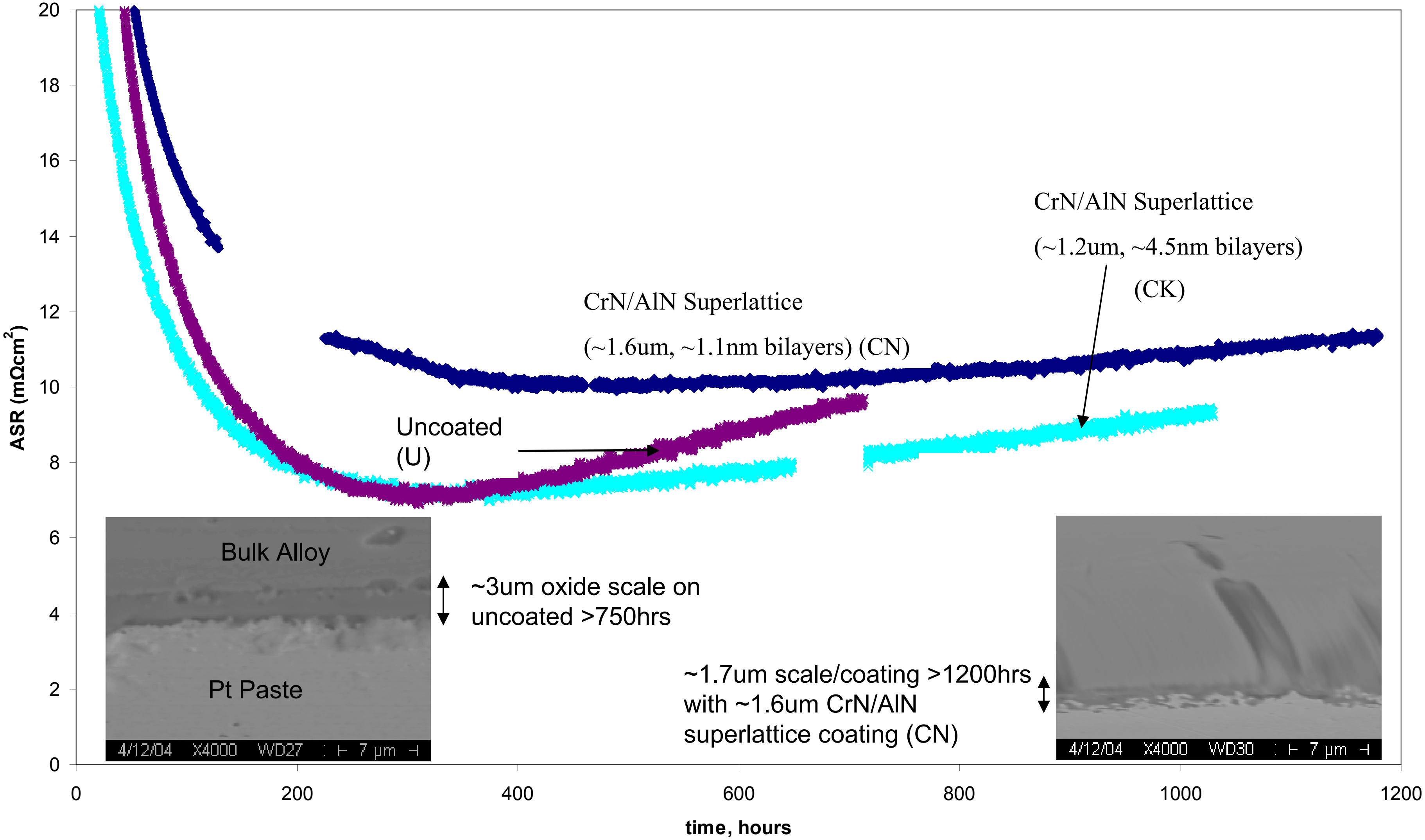




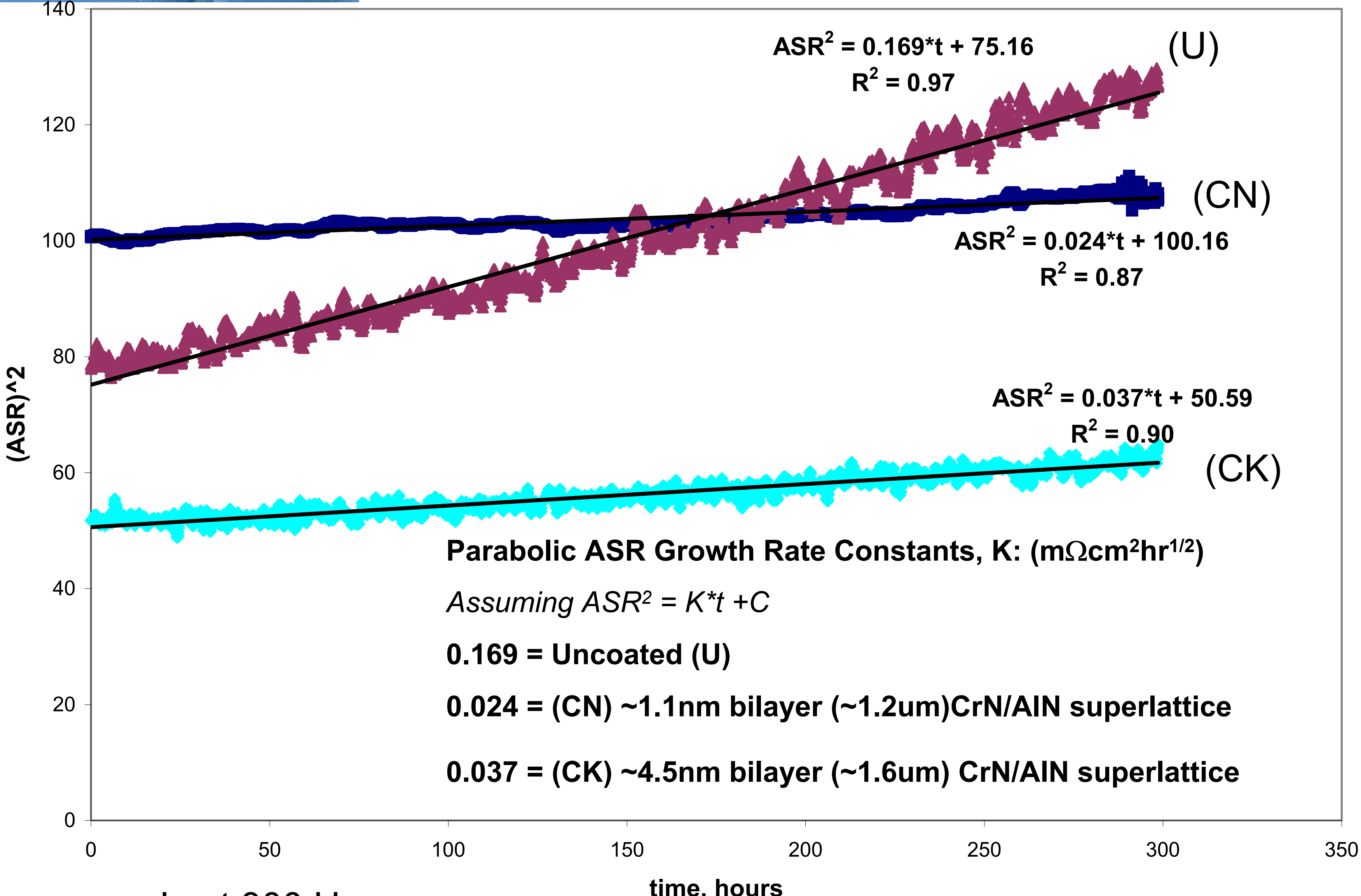
Coating:	CrN Layer Thickness, nm	CrN/AlN bi-layer thickness, nm	Total Thickness, µm (# Repeating Units)	Substrate Steel: X = Results Presented (ID)		
				304	440A	Crofer 22APU
CrN/(CrN/AlN) Multilayer	~10	~1.1	~0.5 (25)		X	
CrN/AlN Superlattice	--	~4.5	~1.6 (360)	X	X	X (CK)
CrN/AlN Superlattice	--	~1.1	~1.2 (1080)	X	X	X (CN)
Uncoated	--	--	--	X	X	X (U)

ASR Results for Crofer 22APU

(Oxidation at 800°C in Air)



ASR Stability



Last 300 Hrs

MONTANA STATE UNIVERSITY BOZEMAN

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