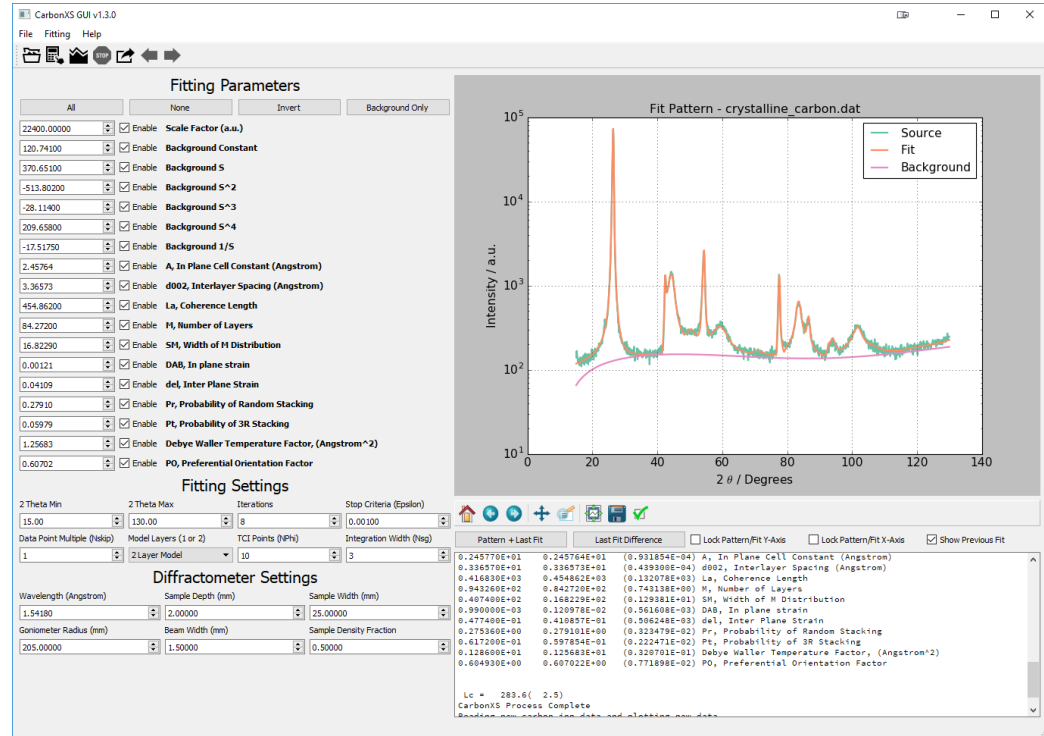




CarbonXS GUI - A Graphical Front End for CarbonXS

Lok-kun Tsui¹ and Fernando Garzon^{1,2}
2016-10-02

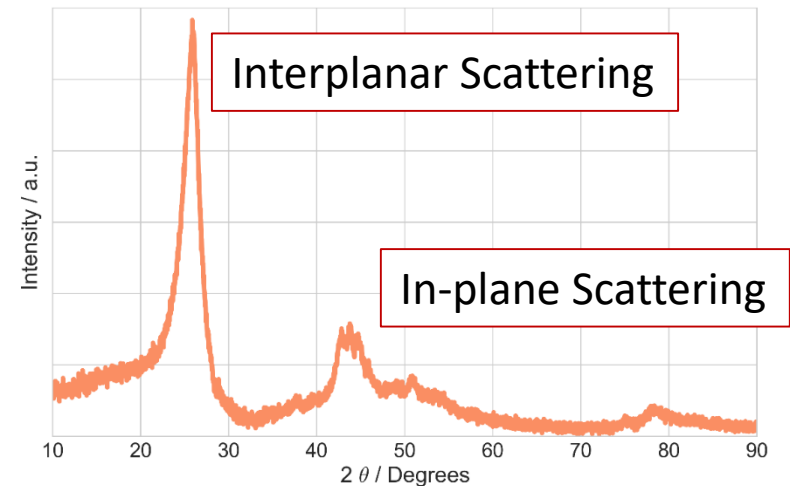
¹Center for Micro-Engineered Materials,
University of New Mexico
²Sandia National Laboratories



- Motivation: X-ray analysis of disordered carbons
- The CarbonXS Model
- CarbonXS GUI
- Examples of using CarbonXS GUI to analyzing non-PGM fuel cell catalysts developed at UNM CMEM

Why X-ray Diffraction for Disordered Carbons?

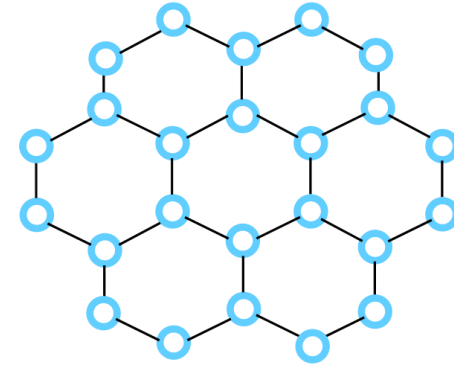
- Disordered carbons are used in a wide variety of applications:
 - Battery and fuel cell electrodes
 - Catalysts and catalyst supports
- Quantitative analysis allows for correlation of structural properties with performance parameters.
- TEM: high resolution imaging and quantitative measurements but limited small spatial sampling extent.
- XRD: Quantitative averaging over the entire sample.



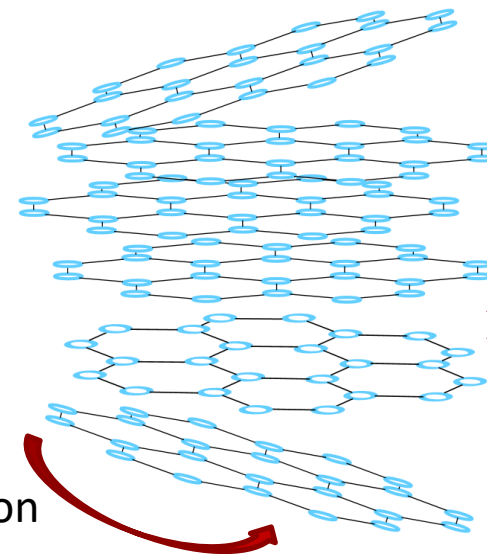
Diffraction pattern
of disordered carbon

Structure of disordered carbons

- Traditional XRD analysis software uses a 3D model when a 2D model is more appropriate for carbon which are composed of stacked sheets.
- Disordered Carbons (DCs): Exhibit random inter-planar shifts and rotations, known as **Turbostratic Disorder**
- Scattering from each grain of carbon originates from multiple sub-grains that scatter incoherently wrapped with high-strain carbon [1, 2].
 - Calculation using traditional Scherrer equation techniques yields smaller than realistic grain sizes.
 - Surface area is much higher compared to BET area.



Hexagonal Graphene Sheet



Rotation

Displacement

Disordered Turbostratic Carbon

1. Franklin, R. E. *Proc. R. Soc. A Math. Phys. Eng. Sci.* **1951**, 209 (1097), 196–218.
2. H. Shi, J. N. Reimers, and J. R. Dahn, *J. Appl. Crystallogr.*, **26**, 827–836 (1993).

The CarbonXS Model

- Calculate scattering from stacked layers of carbon (ordered regions) with a gaussian distribution of random stacking (disordered regions).
- Models the scattering from rods in reciprocal space and integrates the signal observed over all scattering angles.
- **One layer model:** Highly disordered carbons with a distribution of shifts in layer spacing.
- **Two layer model:** Accounts for preferential ABABAB type stacking in highly graphitized carbons. (60%+ graphite)
- Shi implemented this model in software and determined the structural properties of dozens of different types of carbons from heat treatment of petroleum sources [1].
- Subsequently used to study materials for Li-ion batteries [2], coal gasification [3], and FC catalysts [4].

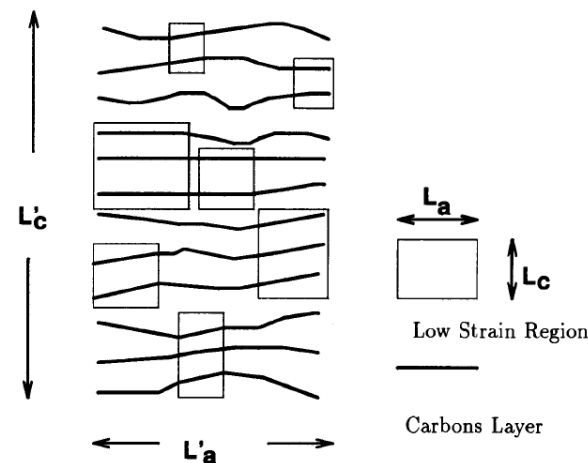
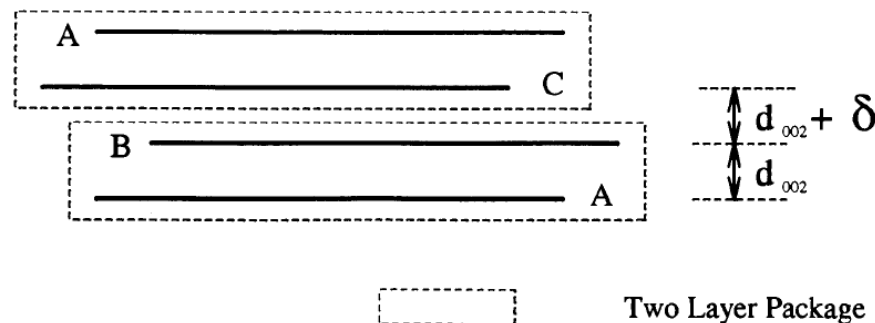


Figure 2.4: Carbon with unorganized and organized regions



Figures: H. Shi, thesis, Simon Fraser University (1993)

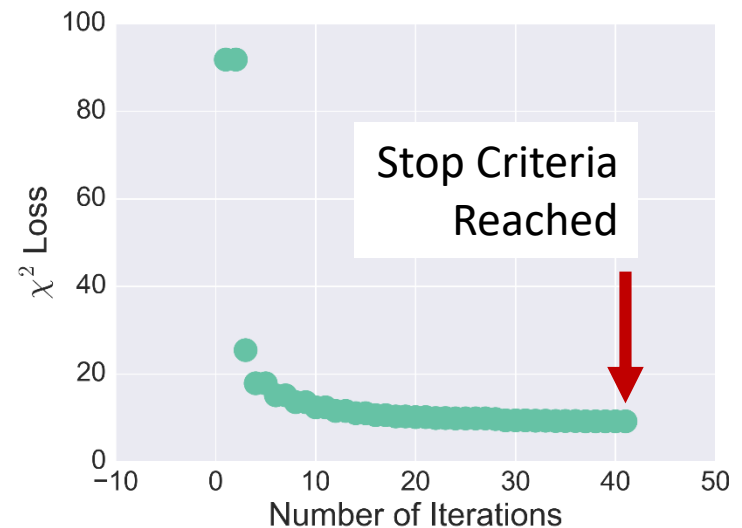
<http://summit.sfu.ca/system/files/iritem1/5690/b1523325x.pdf>

1. H. Shi, J. N. Reimers, and J. R. Dahn, *J. Appl. Crystallogr.*, **26**, 827–836 (1993).
2. Zheng, T.; Reimers, J. N.; Dahn, J. R. *Phys. Rev. B* **1995**, *51* (2), 734–741.
3. Feng, B.; Bhatia, S. K.; Barry, J. C. *Carbon* **2002**, *40* (4), 481–496.
4. Workman, M. J.; Serov, A.; Tsui, L.; Atanassov, P.; Artyushkova, K. *ACS Energy Lett.* **2017**, 1489–1493.

Model Optimization

- Iterative optimization model
- Inputs:
 - Diffraction Pattern $Y(\theta)$
 - Initial Fitting Parameters W_i
 - Diffractometer and sample geometry, radiation wavelength
- Minimize the χ^2 error between the calculated and experimental diffraction patterns.
- Nonlinear optimization of W_i is performed using the Levenberg-Marquardt algorithm.
- For each iteration, stop if $\Delta\chi^2 < \text{user specified } \varepsilon$ or if maximum number of iterations are exceeded.
- Outputs optimized parameters and calculated final pattern.
- Typical runtime: < 20 seconds on a modern CPU (Intel i5).

Fitting Parameters (W_i)
Polynomial Background
Lattice Constants
Lateral Coherence
Number of Layers
Width of layer distribution
In-plane and inter-plane strain
Probability of Random Stacking, 3R Type Stacking
Debye Waller Temperature Factor
Preferential Orientation Factor



CarbonXS (The Fortran Program)



Limitations of CarbonXS:

- Written in 1990s in Fortran 77
- Input and output are both text.
Requires separate plotting program.
- Diffraction geometry, fit settings, optimization parameters are tightly coupled.
- XRD data files must be configured to the expected format.
- Command line only.

Objectives for CarbonXS GUI:

- Provide a graphical interface for CarbonXS.
- Improve UI and UX.
- Get it to run on modern platforms.
- Support importing of typical XRD data files.
- Minimal modification to CarbonXS other than compatibility and bug fixes – Preserve numerical reproducibility.

```
MINGW64:/c:/Users/LKTSUI/Dropbox/research/programs/CarbonXSGui/versions...
C
LKTSUI@LKTSUI-PC MINGW64 ~/Dropbox/research/programs/CarbonXSGui/versions/Carbon
XSGui_v1.3.1-windows (master)
$ cd carbonxs

LKTSUI@LKTSUI-PC MINGW64 ~/Dropbox/research/programs/CarbonXSGui/versions/Carbon
XSGui_v1.3.1-windows/carbonxs (master)
$ ls
carbon.cmn  carbon.out          compiling.txt         libwinpthread-1.dll*
carbon.dat  CARBONXS.FOR         libgcc_s_seh-1.dll*  SCAN.DAT
carbon.inp  carbonxs_gFortran.exe* libquadmath-0.dll*

LKTSUI@LKTSUI-PC MINGW64 ~/Dropbox/research/programs/CarbonXSGui/versions/Carbon
XSGui_v1.3.1-windows/carbonxs (master)
$ ./carbonxs_gfortran.exe
Title in data file :No title in your data file!!!
Data File name :SCAN.DAT                      Lambda : 1.54180
# of raw data pts : 2001                       Raw theta limits : 10.00 to 90.00
# of data pts used : 2001                     Theta limits used : 10.00 to 90.00
Max # of it's : 100                           Min delta Chi^2 : 0.00100
# of pts in TCI : 10                          TCI range : +/- 3 Sigma
Relative Density : 0.500                      Stacking Model : 1 layer
Goniometer Radius :205.000(mm)                X-ray Beam Width : 1.500(mm)
Sample Well Depth : 2.000(mm)                 Sample Well Width : 25.000(mm)

Iter #    Chi^2      Alambda
1         .64942E+01  0.10E-01
2         .64665E+01  0.10E-02
3         .63727E+01  0.10E-03
4         .63727E+01  0.10E-02
5         .63727E+01  0.10E-01
6         .62626E+01  0.10E-02
7         .62626E+01  0.10E-01
8         .62626E+01  0.10E+00
9         .62626E+01  0.10E+01
10        .62626E+01  0.10E+02
11        .62604E+01  0.10E+01

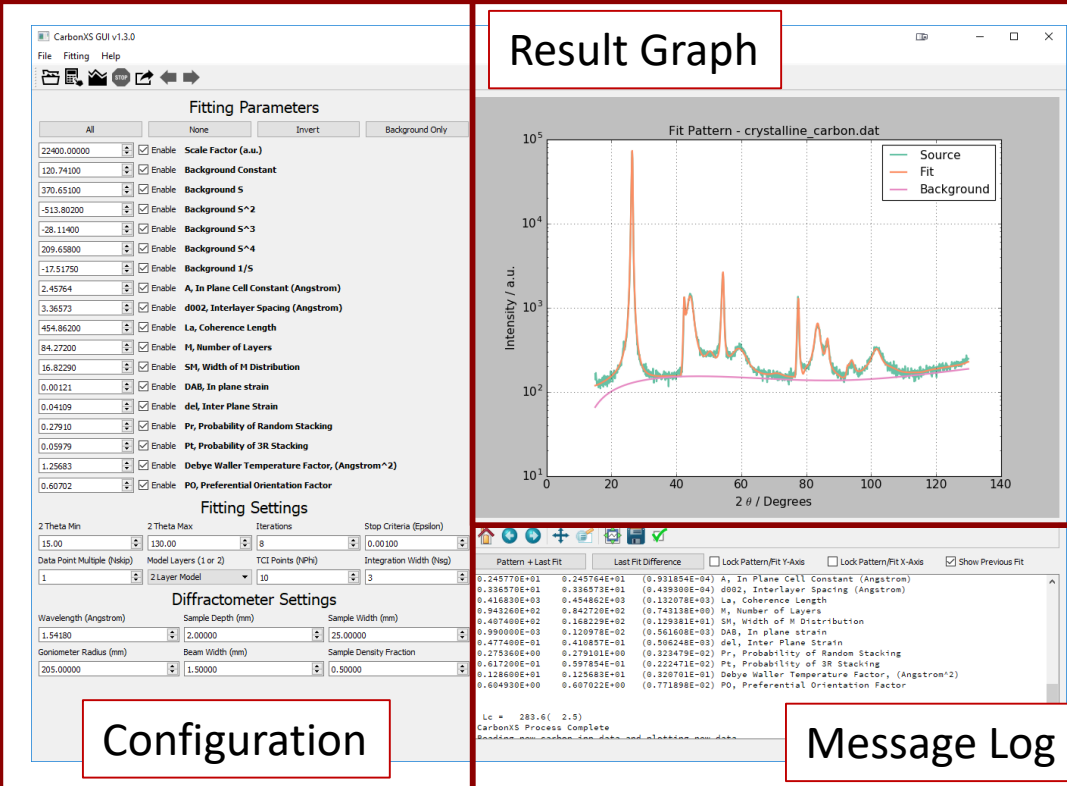
Final Parameters
Old Value  New Value      (esd)      Description
0.469000E+05  0.515723E+05  (0.465523E+05) Scale Factor (a.u.)
0.801724E+04  0.835931E+04  (0.324566E+03) Background Constant
-.459593E+04  -.551100E+04  (0.179214E+04) Background S
-.317152E+04  -.292205E+04  (0.441575E+04) Background S^2
0.777594E+03  0.189472E+04  (0.491679E+04) Background S^3
0.304651E+04  0.227382E+04  (0.201962E+04) Background S^4
0.372066E+02  0.189339E+02  (0.236459E+02) Background 1/S
0.243224E+01  0.243283E+01  (0.985751E-03) A, In Plane Cell Constant (Angstro
m)
0.342658E+01  0.342573E+01  (0.338271E-03) d002, Interlayer Spacing (Angstrom
)
0.318558E+03  0.282656E+03  (0.250096E+03) La, Coherence Length
0.885524E+02  0.108864E+03  (0.254755E+02) M, Number of Layers
```

CarbonXS on the Command Line

CarbonXS GUI – Version 1.3.1 (June 2017)



- Recompiled with GNU GFortran, a modern Fortran compiler for modern operating systems.
- Powered by:  python  PySide Python for Qt
- Crossplatform¹: Windows, Linux, Mac OSX
- Available for free on our Github page
- Open Source Software



The screenshot displays the CarbonXS GUI v1.3.0 interface, divided into three main sections:

- Configuration:** The left panel shows various fitting parameters and settings. The "Fitting Parameters" section includes a table of parameters such as Scale Factor (a.u.), Background Constant, and Background S, with checkboxes to enable or disable them. Below this, the "Fitting Settings" section includes fields for 2 Theta Min/Max, Iterations, and Stop Criteria (Epsilon). The "Diffractometer Settings" section includes fields for Wavelength (Angstrom), Sample Depth (mm), Sample Width (mm), Goniometer Radius (mm), Beam Width (mm), and Sample Density Fraction.
- Result Graph:** The top right panel, titled "Fit Pattern - crystalline_carbon.dat", shows a plot of Intensity / a.u. versus 2θ / Degrees. The plot displays the source data (green line), the fit (orange line), and the background (pink line). The y-axis is logarithmic, ranging from 10¹ to 10⁵.
- Message Log:** The bottom right panel shows a list of fit parameters and their values, including A, In Plane Cell Constant (Angstrom), d002, Interlayer Spacing (Angstrom), La, Coherence Length, N, Number of Layers, SM, Width of H Distribution, DAB, In plane strain, del, Inter Plane Strain, Pr, Probability of Random Stacking, Pt, Probability of 3R Stacking, Debye Waller Temperature Factor, (Angstrom⁻²), and PO, Preferential Orientation Factor.

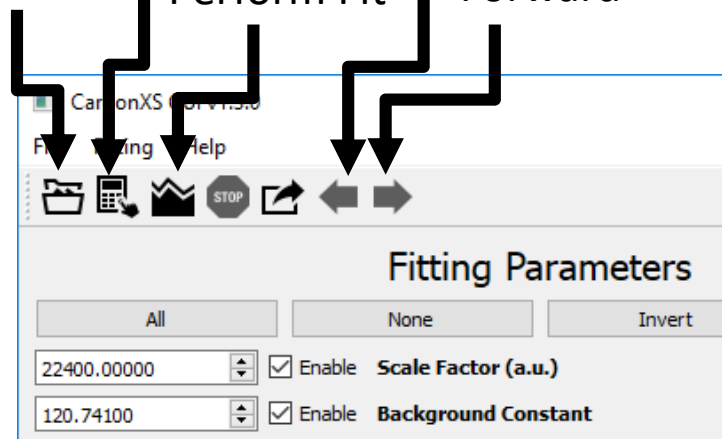
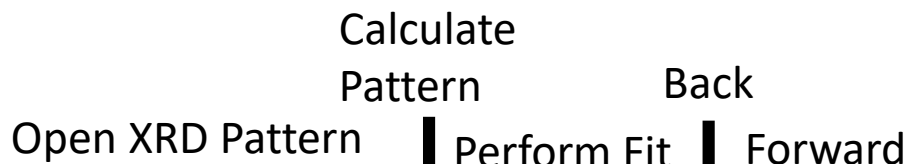
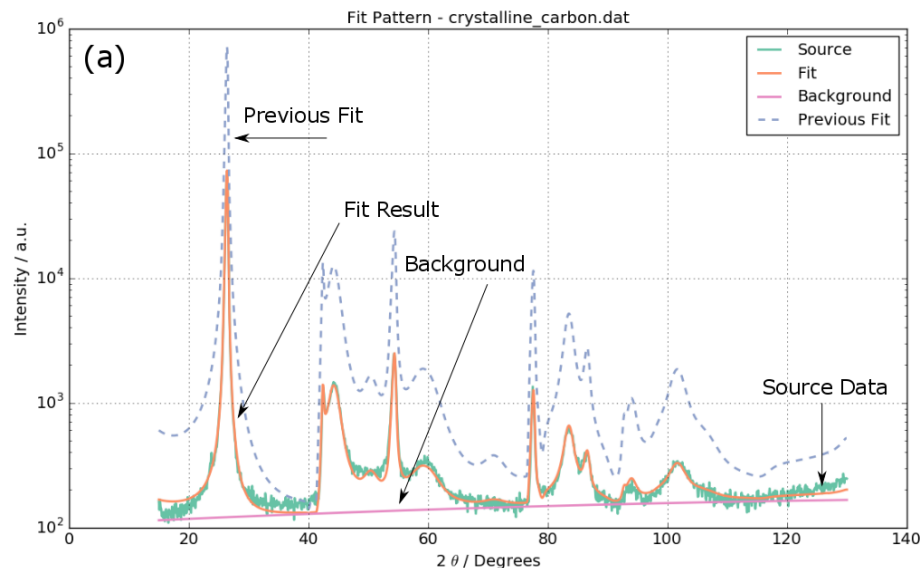
Download at https://github.com/lktsui/carbon_xs_gui
Documentation at https://lktsui.github.io/carbon_xs_gui

¹ Systems Tested: Windows 7 & 10, Ubuntu & Fedora Linux, Mac OSX 10.10, 10.11, 10.12

New Features of CarbonXS GUI

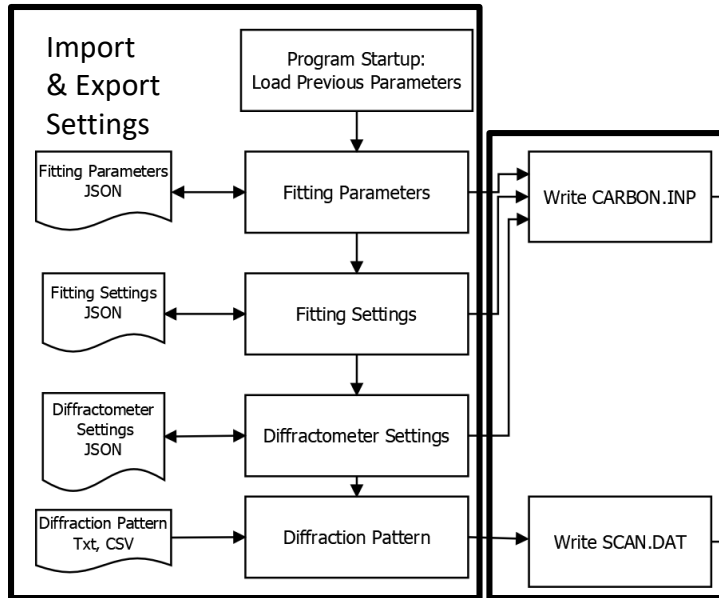


- **Graphing:** Showing the original data, background function, and fit result without needing a separate plotting software.
- **Calculation Mode:** Simulate diffraction pattern without needing to perform a fit. Useful for parameter adjustment.
- **Decoupled Configuration Files:** Exports and imports parameters, fit settings, and diffractometer settings from JSON data files for easier data exchange.
- **Fit calculation buffer:**
 - Undo a bad fit.
 - Step back and forth between fit results.
- **Import formats supported:**
 - 2 column data, Jade MDI format, Rigaku RAS, X-Y
- **Input Checking:** Alerts the user if they are inputting nonsensical parameters.



Flowchart of Optimization Mode

carbonxs_gui (Python)

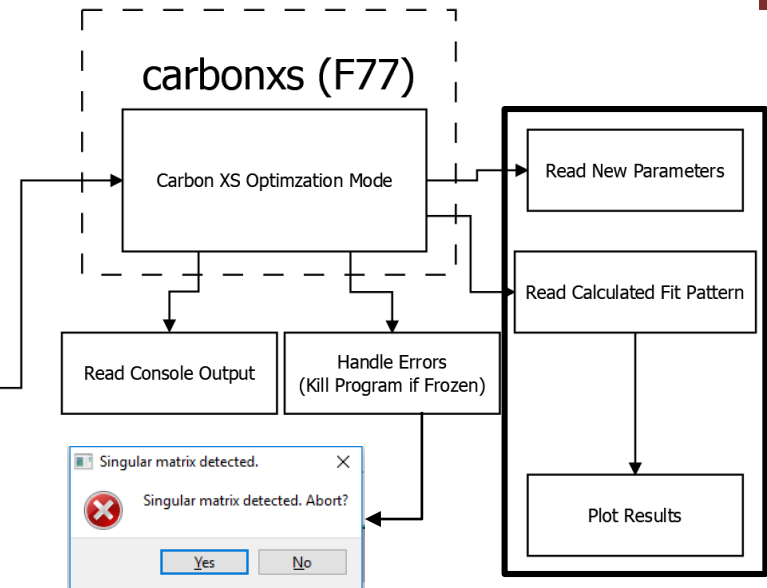


1. Setup Phase

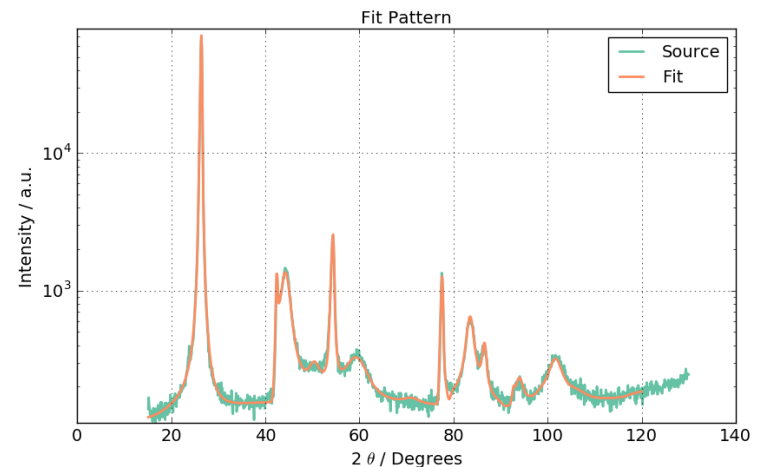
2. Automatically Generate CarbonXS Inputs

Fitting Parameters	
All	None
22400.00000	<input checked="" type="checkbox"/> Enable Scale Factor (a.u.)
120.74100	<input checked="" type="checkbox"/> Enable Background Constant
370.65100	<input checked="" type="checkbox"/> Enable Background S
-513.80200	<input checked="" type="checkbox"/> Enable Background S ²
-28.11400	<input checked="" type="checkbox"/> Enable Background S ³
209.65800	<input checked="" type="checkbox"/> Enable Background S ⁴
-17.51750	<input checked="" type="checkbox"/> Enable Background 1/S
2.45764	<input checked="" type="checkbox"/> Enable A, In Plane Cell Constant (Angstrom)
3.36573	<input checked="" type="checkbox"/> Enable d002, Interlayer Spacing (Angstrom)
454.86200	<input checked="" type="checkbox"/> Enable La, Coherence Length
84.27200	<input checked="" type="checkbox"/> Enable M, Number of Layers
16.82290	<input checked="" type="checkbox"/> Enable SM, Width of M Distribution
0.00121	<input checked="" type="checkbox"/> Enable DAB, In plane strain
0.04109	<input checked="" type="checkbox"/> Enable del, Inter Plane Strain
0.27910	<input checked="" type="checkbox"/> Enable Pr, Probability of Random Stacking
0.05979	<input checked="" type="checkbox"/> Enable Pt, Probability of 3R Stacking
1.25683	<input checked="" type="checkbox"/> Enable Debye Waller Temperature Factor, (Angstrom ²)
0.60702	<input checked="" type="checkbox"/> Enable PO, Preferential Orientation Factor

3. Fortran Code Called

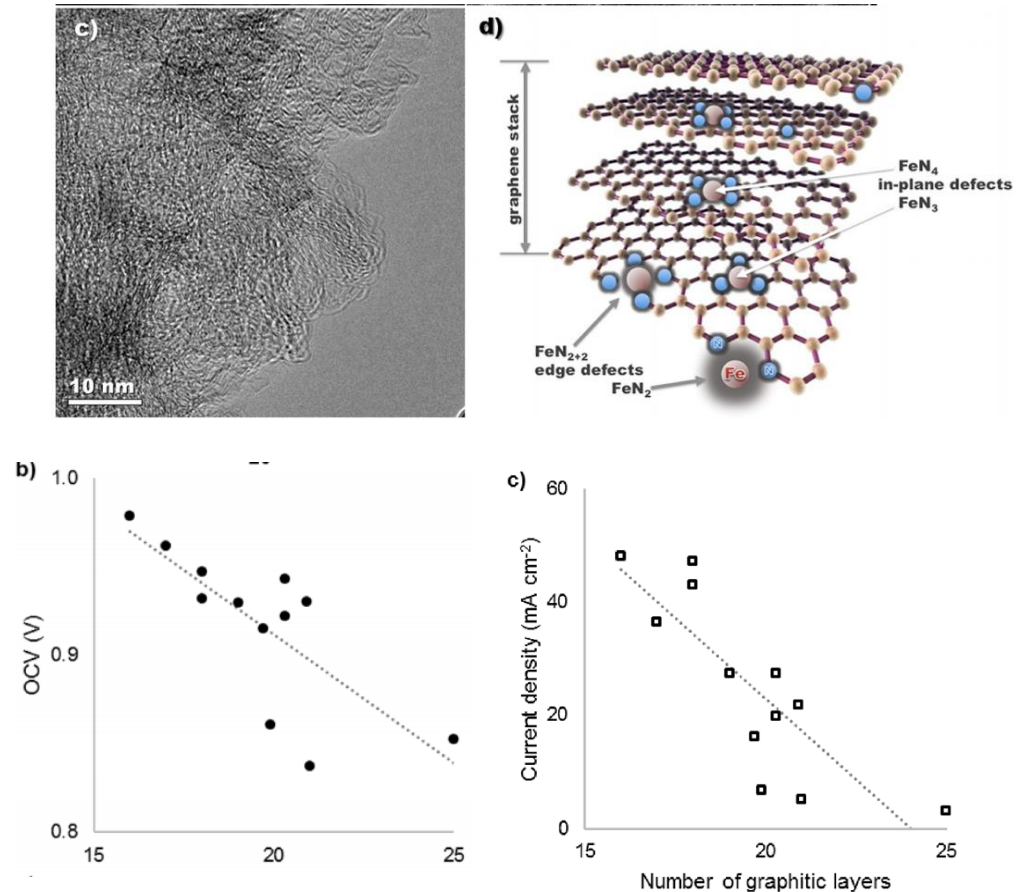


4. Obtain Results



Influence of number of layers on catalytic activity

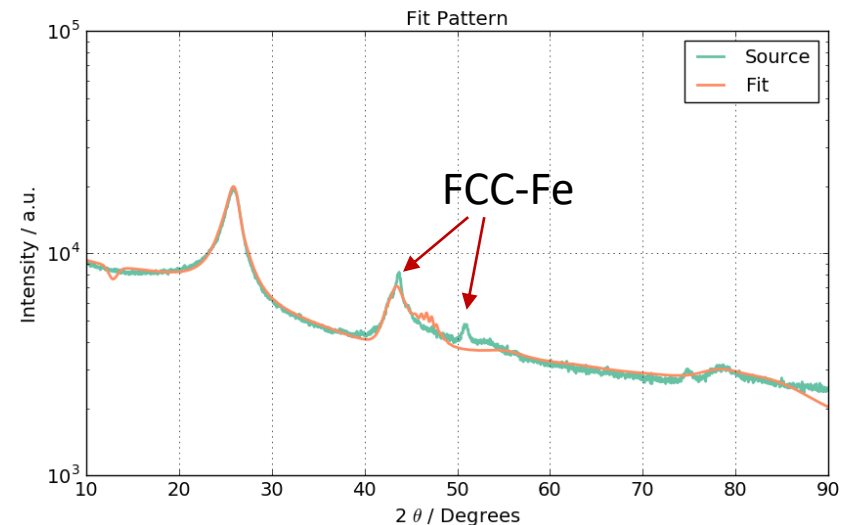
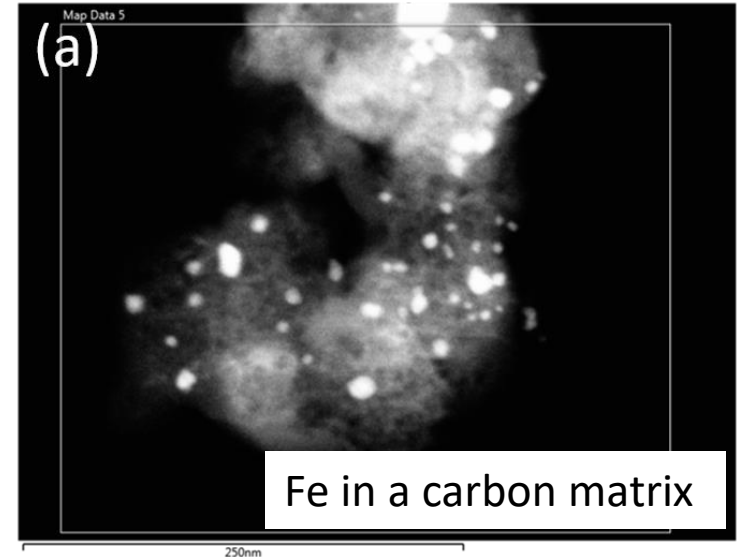
- **Motivation:** Non-PGM catalysts for less expensive fuel cell catalysts than Pt.
- High surface area Fe-N-C catalyst was synthesized by pyrolysis of organic and metal-salt precursors.
- Fewer coherent layers yielded higher current density at a test potential and OCV.
- Implied that active sites were on the plane rather than edges of plates.
- Fewer layers meant more planar area exposed per unit mass.



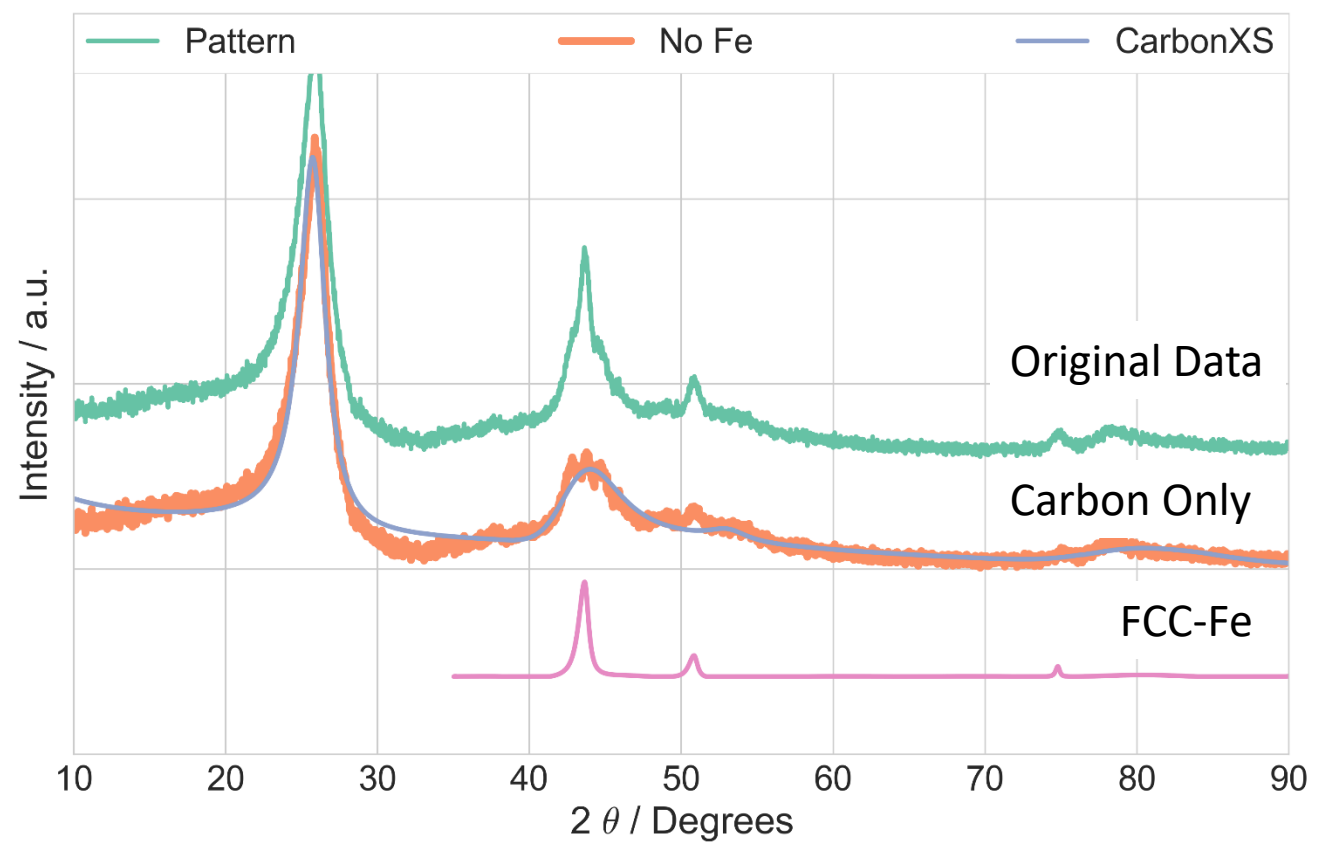
From: M. J. Workman, A. Serov, L. Tsui, P. Atanassov, and K. Artyushkova, *ACS Energy Lett.*, 1489–1493 (2017)

Dual Refinement: Carbon + Metal

- Catalyst prepared by hydrothermal synthesis with Fe particles embedded in a carbon matrix.
- CarbonXS cannot directly be used to analyze materials containing both carbon and metal phases.
- Dual refinement procedure:
 - Treat the carbon signal as background and use JADE to perform whole pattern fitting for the metal phase.
 - Subtract the metal peaks to obtain the residual carbon pattern.
 - Perform the carbon analysis with CarbonXS GUI



Improved fit to carbon peaks after removing Fe



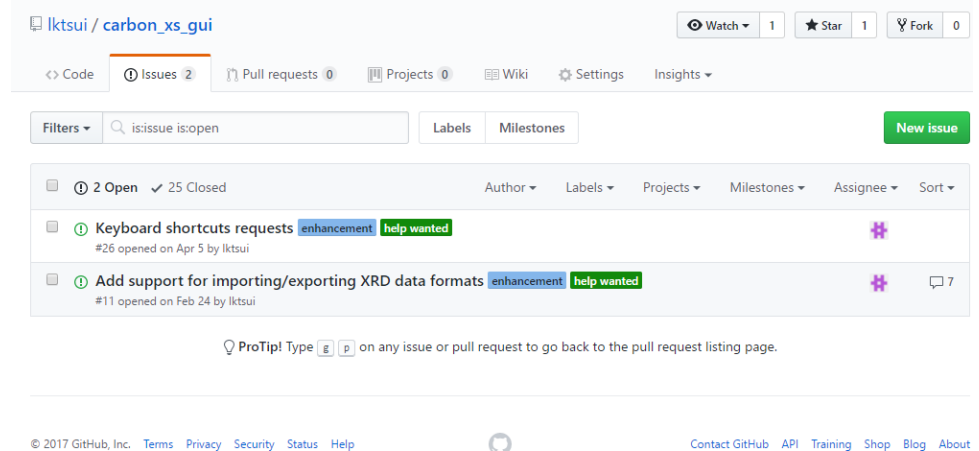
Fit results (Dual Refinement)

FCC-Fe
Lattice parameter: 3.59Å
Crystallite size: 12 nm

Carbon
Lateral coherence: 50 nm
Vertical coherence: 18 nm

Conclusions

- We have developed a graphical interface to CarbonXS, significantly lowering the barrier to use for researchers.
- We have demonstrated its application to materials of interest in the field of non-PGM fuel cell catalysts.
- A dual refinement procedure was used for a metal-carbon mixture.
- We invite users to submit requests for features, bug reports, and code contributions to our Github page.



lktsui / carbon_xs_gui

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#26 opened on Apr 5 by lktsui							
Add support for importing/exporting XRD data formats	enhancement help wanted						7
#11 opened on Feb 24 by lktsui							

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https://github.com/lktsui/carbon_xs_gui/

Acknowledgments

- Original Developers of CarbonXS and Permission to Continue work: H. Shi, J.N. Reimers, J. Dahn.
- Testing: Michael Workman and Mark McArthur
- Funding: