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CarbonXS GUI - A Graphical Front End for CarbonXS

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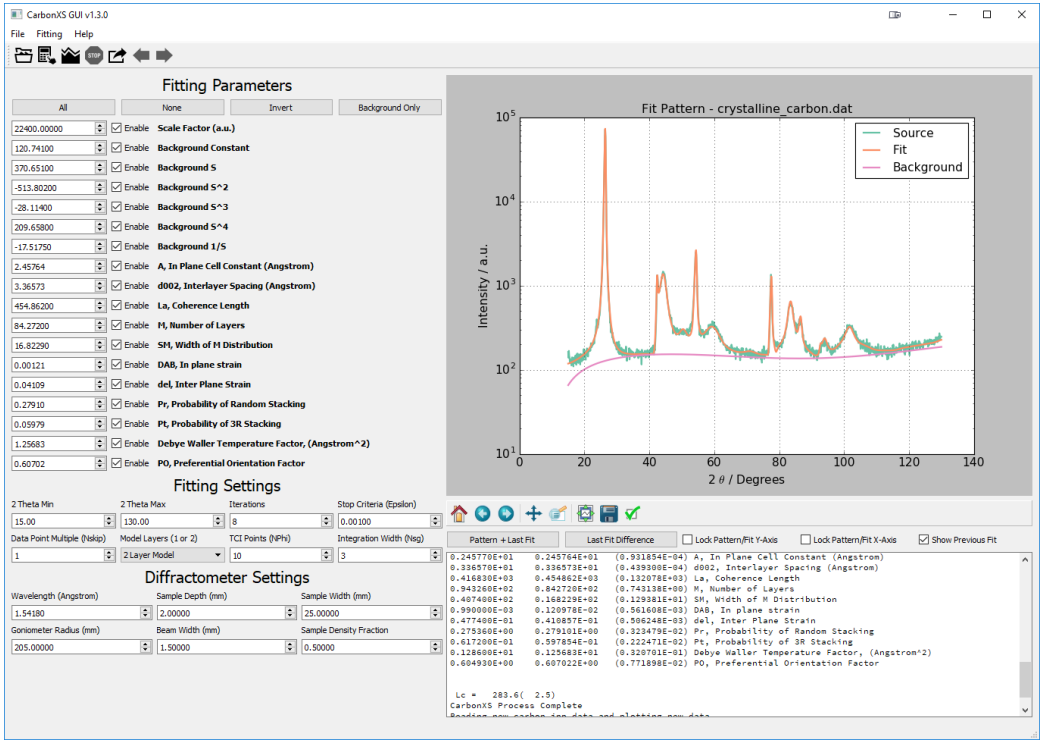

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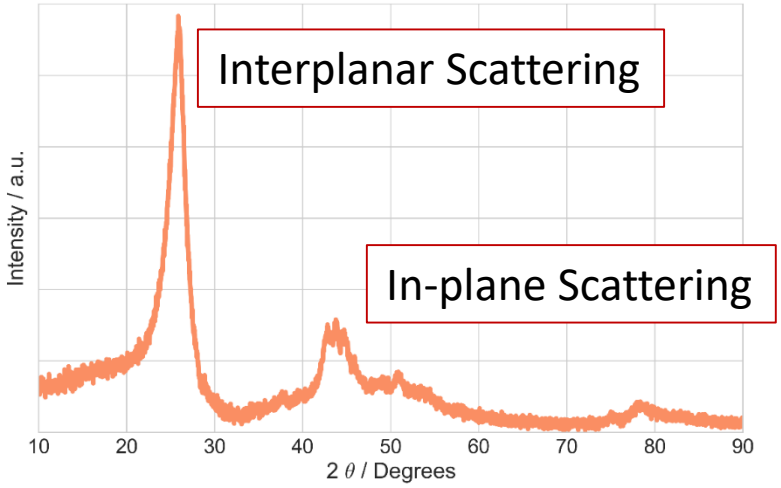
Outline

- 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?

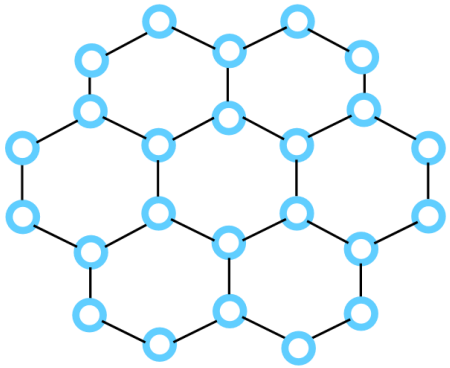
- Disordered carbons are used in a wide variety of applications:
  - Battery and fuel cell electrodes
  - Catalysts and catalyst supports
- Quantitative analysis allows for correlation of structural properties with performance parameters.
- TEM: high resolution imaging and quantitative measurements but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



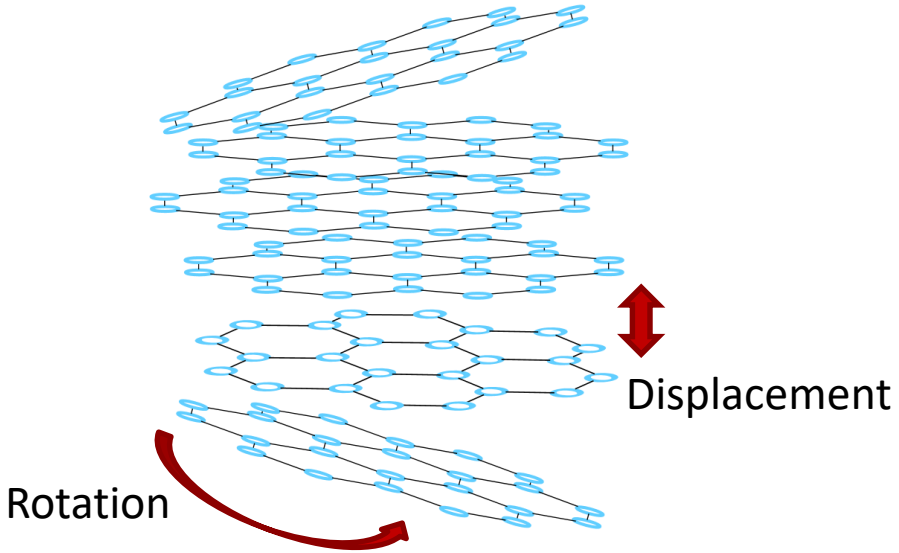
Diffraction pattern of disordered carbon

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



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].

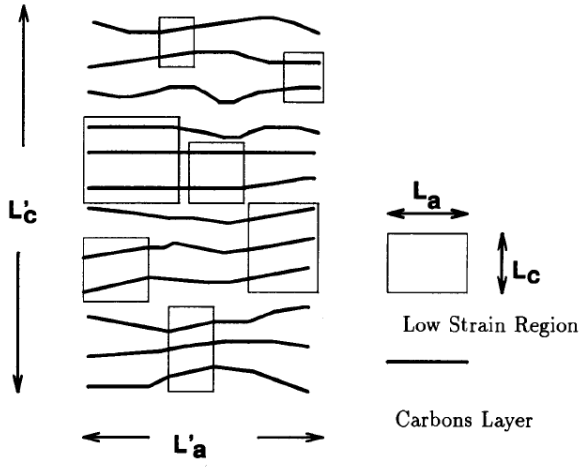
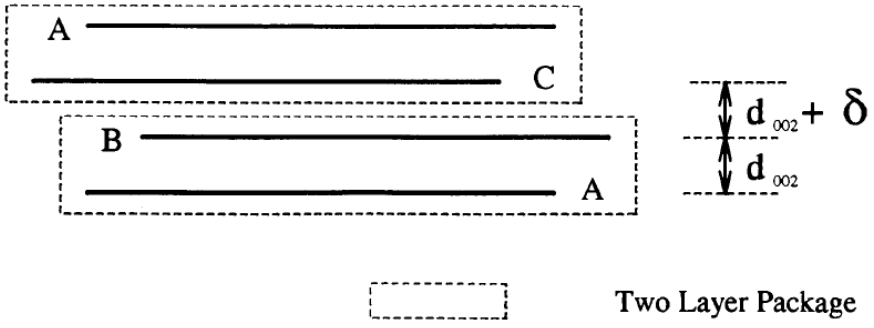


Figure 2.4: Carbon with unorganized and organized regions



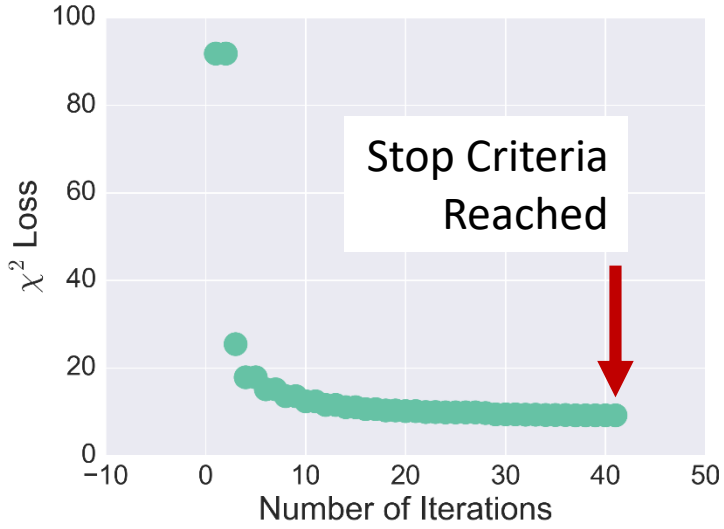
Figures: H. Shi, thesis, Simon Fraser University (1993)
http://summit.sfu.ca/system/files/iritems1/5690/b1523325x.pdf.

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 $\Delta\chi^2$ < user specified ε 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



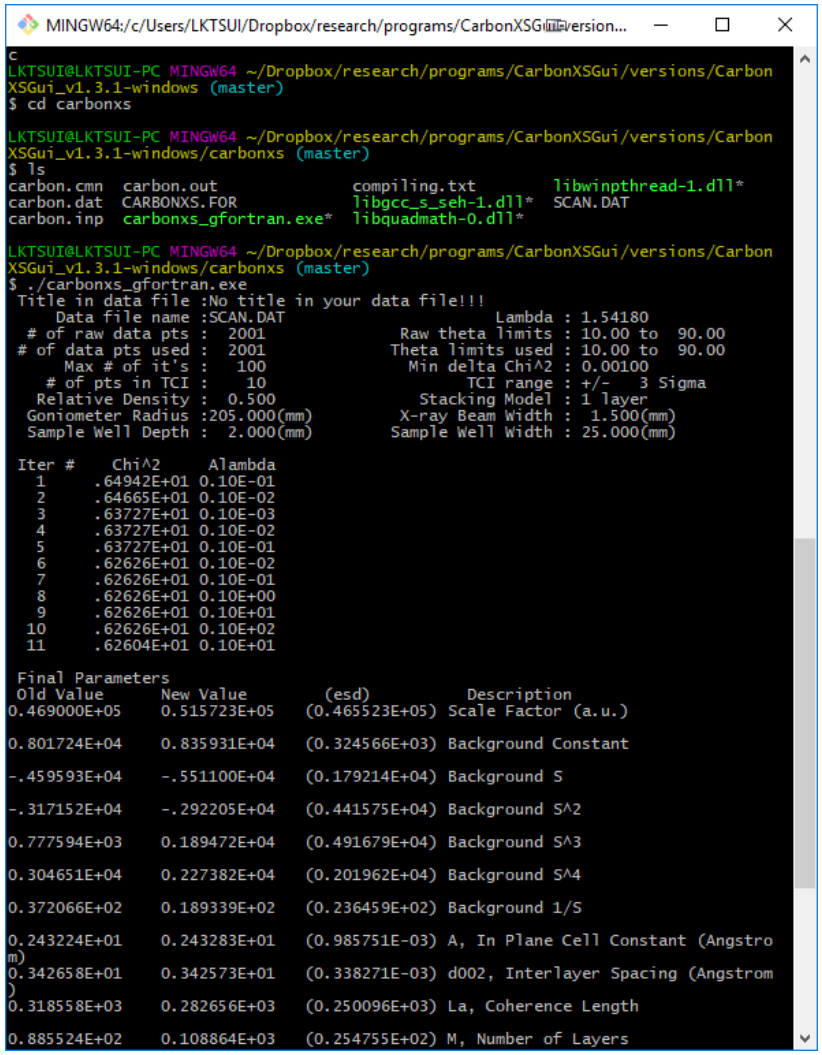
CarbonXS (The Fortran Program)

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:

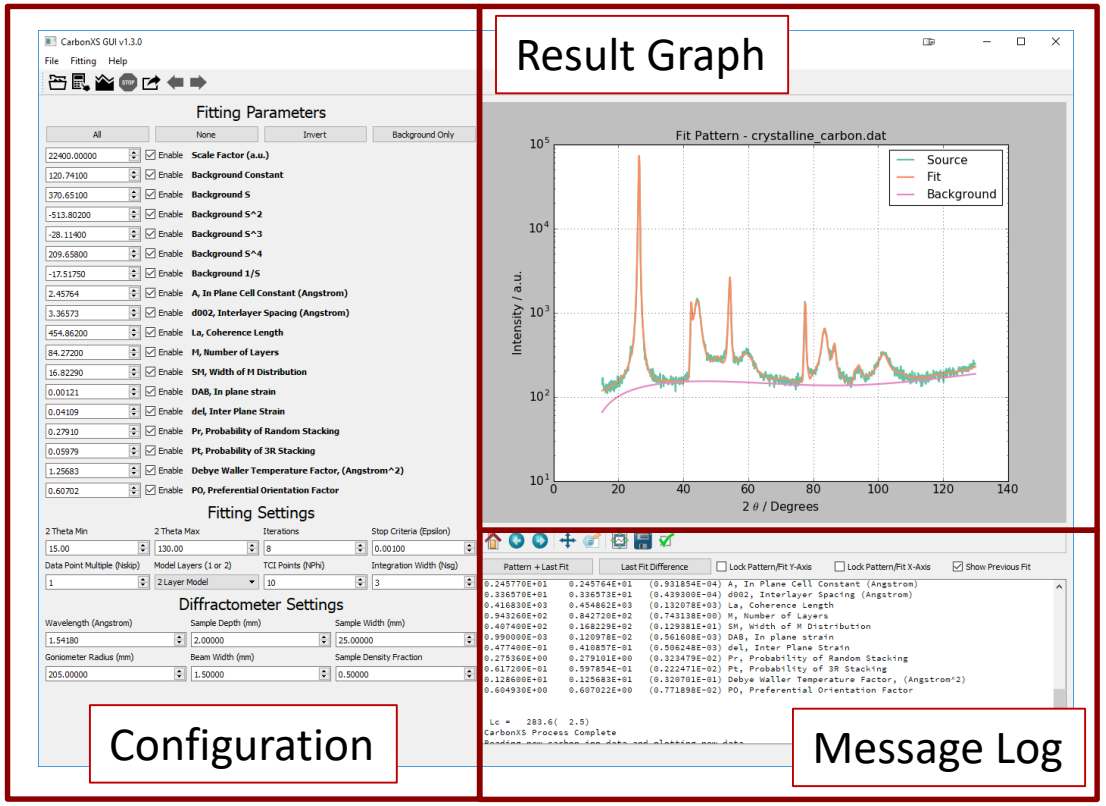
- Provide a graphical interface for CarbonXS.
- Improve UI and UX.
- Get it to run on modern platforms.
- Support importing of typical XRD data files.
- Minimal modification to CarbonXS other than compatibility and bug fixes – Preserve numerical reproducibility.



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
- Crossplatform[1]: Windows, Linux, Mac OSX
- Available for free on our Github page
- Open Source Software

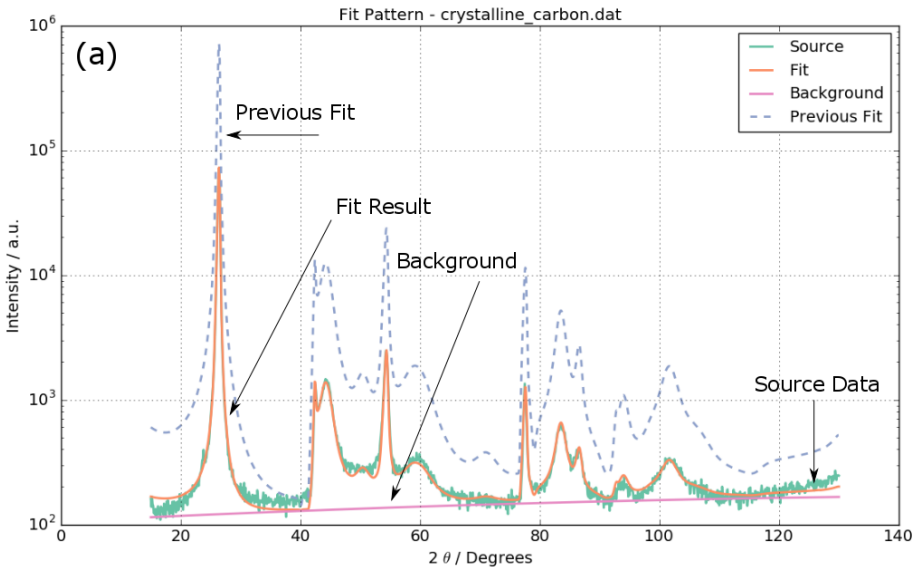


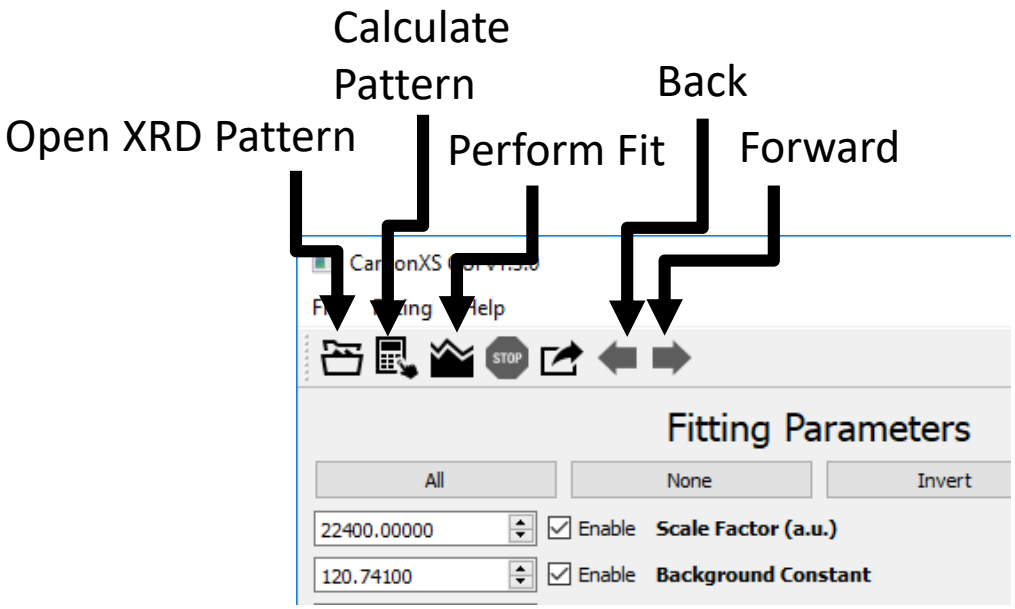
Download at https://github.com/lktsui/carbon_xs_gui
Documentation at https://lktsui.github.io/carbon_xs_gui

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

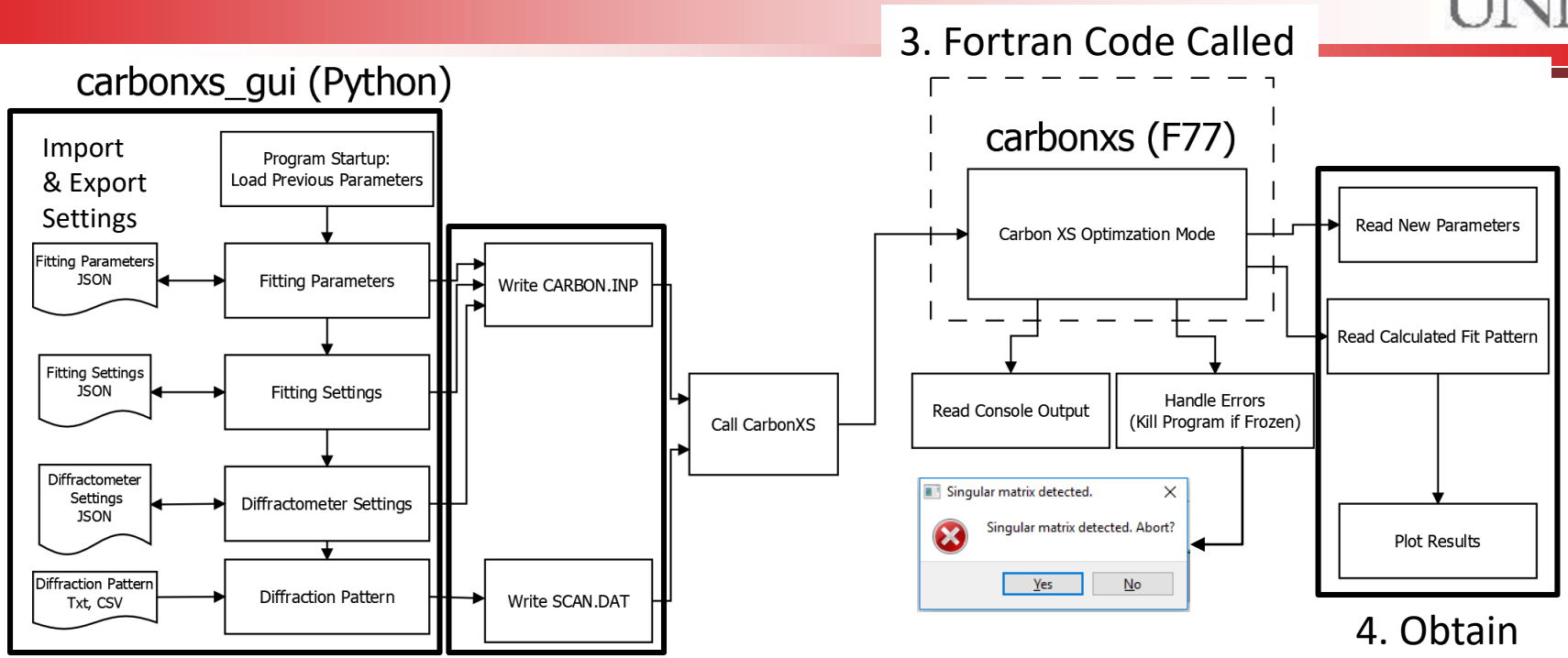
New Features of CarbonXS GUI

- **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.

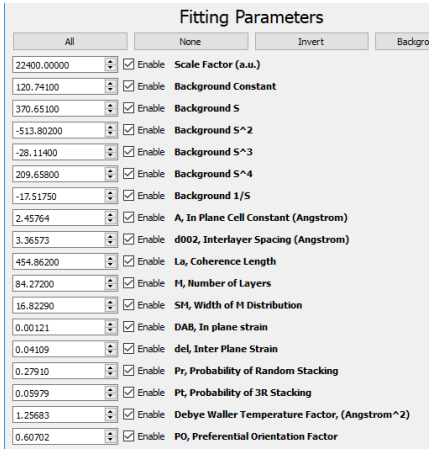




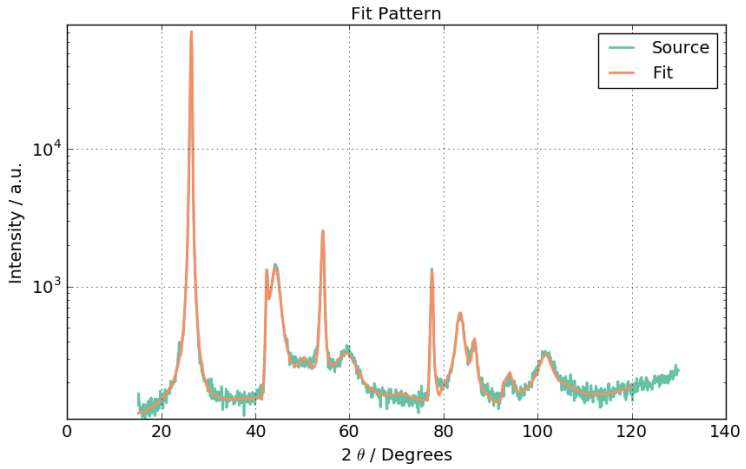
Flowchart of Optimization Mode



1. Setup Phase

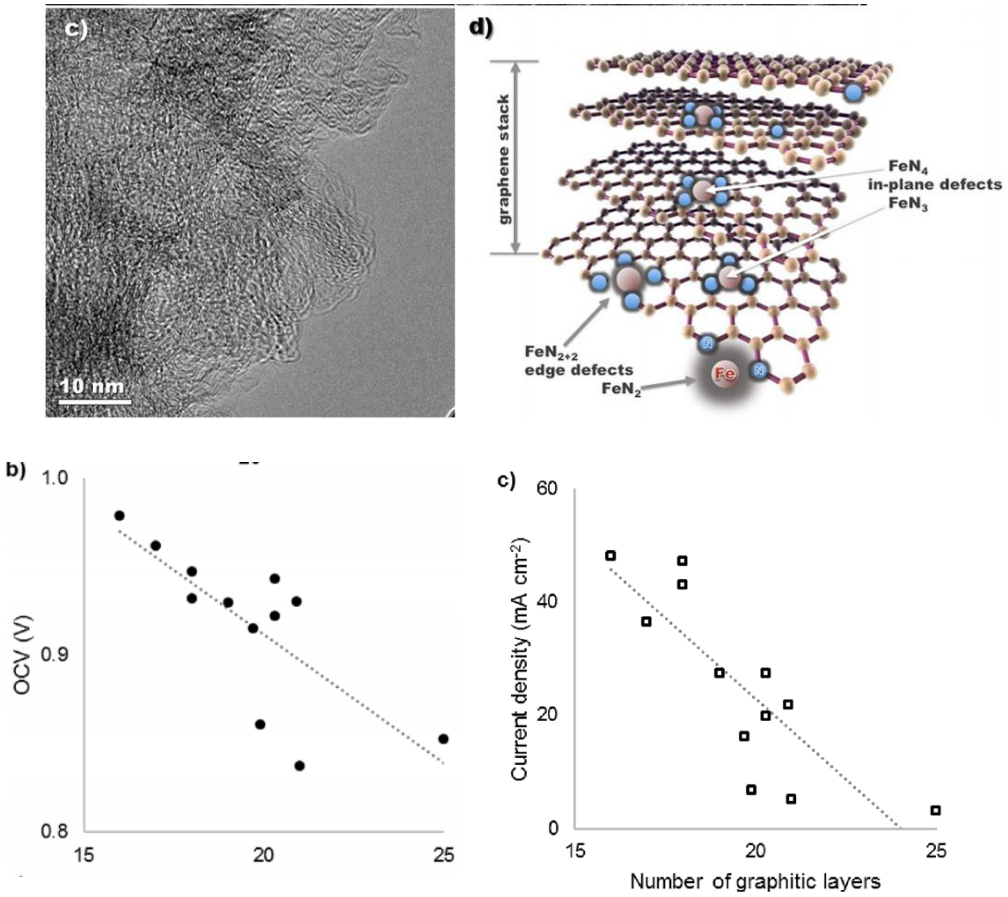


2. Automatically Generate CarbonXS Inputs



Influence of number of layers on catalytic activity

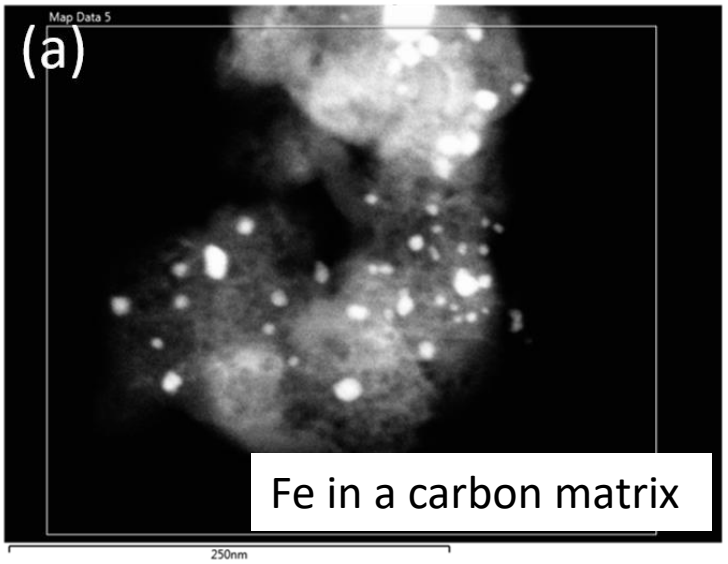
- **Motivation:** Non-PGM catalysts for less expensive fuel cell catalysts than Pt.
- High surface area Fe-N-C catalyst was synthesized by pyrolysis of organic and metal-salt precursors.
- Fewer coherent layers yielded higher current density at a test potential and OCV.
- Implied that active sites were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

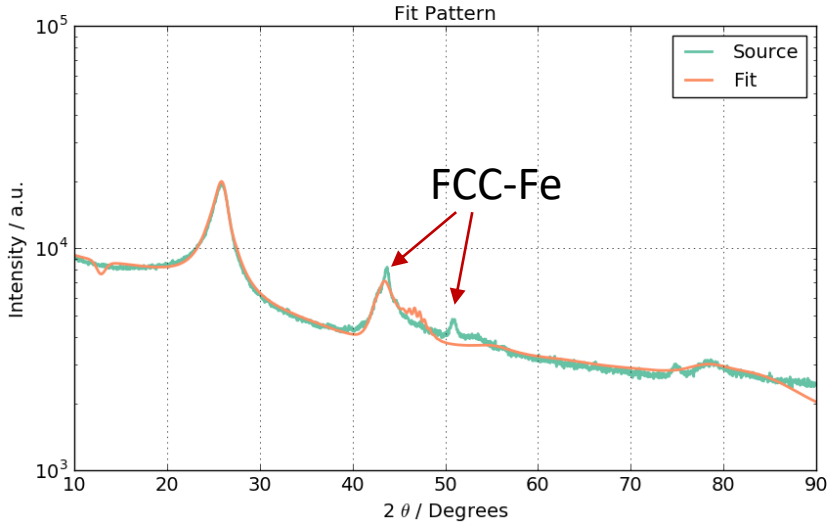


From: M. J. Workman, A. Serov, L. Tsui, P. Atanassov, and K. Artyushkova, *ACS Energy Lett.*, 1489–1493 (2017)

Dual Refinement: Carbon + Metal

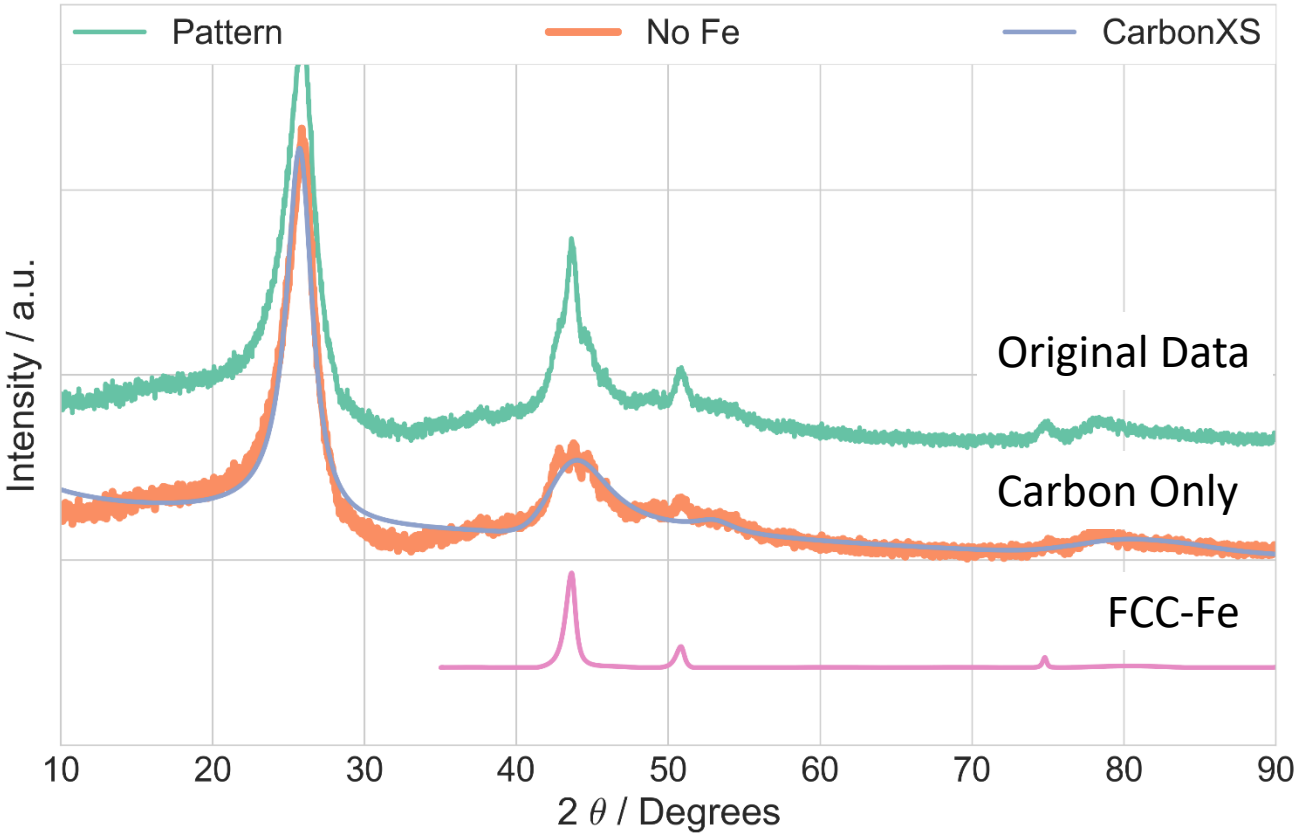
- Catalyst prepared by hydrothermal synthesis with Fe particles embedded in a carbon matrix.
- CarbonXS cannot directly be used to analyze materials containing both carbon and metal phases.
- Dual refinement procedure:
  - Treat the carbon signal as background and use JADE to perform whole pattern fitting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





From: R. Gokhale, L. Tsui, K. Roach, Y. Chen, M.M. Hossen, K. Artyushkova, F. Garzon, P. Atanassov, "Hydrothermal synthesis of platinum group metal-free catalysts: structural elucidation and oxygen reduction catalysis." Submitted.

Improved fit to carbon peaks after removing Fe



Fit results (Dual Refinement)

FCC-Fe

Lattice parameter: 3.59Å

Crystallite size: 12 nm

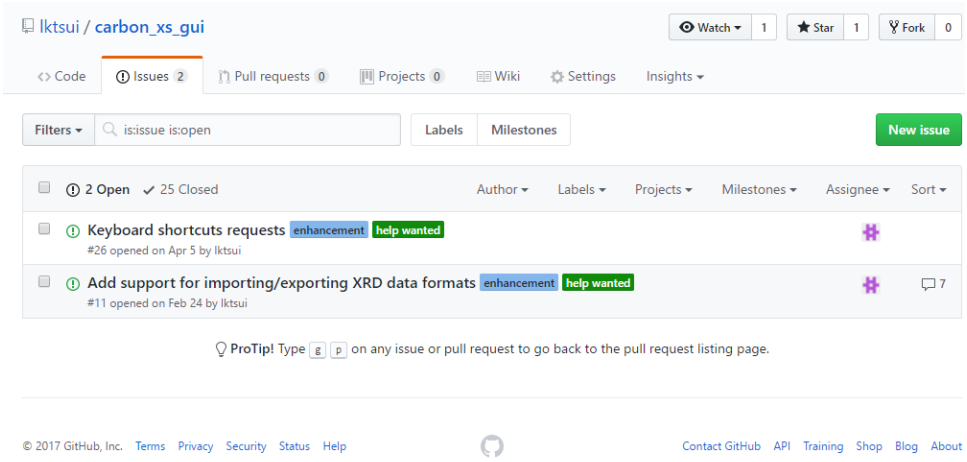
Carbon

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.



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:

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