A Review of Problems With Measurements of L_c in Carbon Materials

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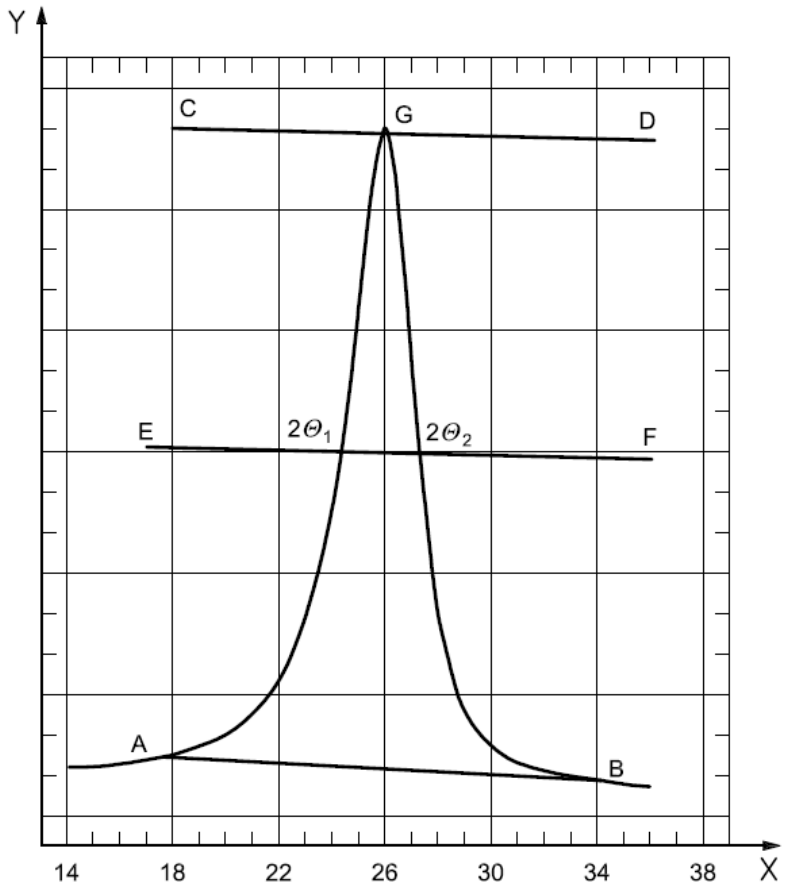
Why L_c Measurements ?

- Carbon is best material to use for many applications
  - High thermal resistance
  - Electrically conducting
  - Reactivity can be adjusted to be both high or low
  - Strength can be adjusted to be both high or low
- Carbon is often used as electrochemical electrodes
  - Aluminium production (both anode and cathodes)
  - Batteries
- Properties of pure carbon is mainly given by the structure
  - Determines electrical and reactivity properties
- Structure can be characterized by X-Ray Diffraction (XRD)
  - d_{002} (interlayer distance), L_c (crystallite height)
  - L_a (crystallite diameter)
  - Cheap, straight-forward, routine measurements

ISO and ASTM Standards

- ASTM D5187-91 (2010): Standard Test Method for Determination of Crystallite Size (L_c) of Calcined Petroleum Coke by X-Ray Diffraction
- ISO 20203 (2005): Carbonaceous materials used in the production of aluminium — Calcined coke — Determination of crystallite size of calcined petroleum coke by X-ray diffraction
- Based on powder X-ray diffraction
- Specifies method
  - sample preparation
  - how to interpret the X-ray pattern
  - how to calculate the L_c value

ISO 20203: Determination of L_c value



- **9.1.2** "Determine the average low and high backgrounds (Points A and B, respectively) on the diffraction scan and connect them with a straight line."
- **9.1.3** "Construct line CD parallel to line AB, and going through the apex of the peak at point G [(*hkl* (002) at 0,335 nm]. Draw the line such that, if the peak is irregular, it will pass through the average of the irregularities."

ISO 20203: Determination of L_c value

- **9.1.4 "**Determine the full-width half maximum (FWHM) of line AB. Construct line EF such that it intersects the peak at half of its maximum value. The points at which EF intersects the peak are $2\Theta_1$ and $2\Theta_2$, respectively."
- **9.1.5 "**For computer simulation based on the intensities recorded at 0.2° intervals, produce a mathematical representation of the diffraction curve. Determine the baseline, peak, peak height, and half-peak height to produce the half-peak height angles, $2\Theta_1$ and $2\Theta_2$, as above."

- **9.2** Determine the mean crystallite height L_c (derived from Scherrer equation)

$$\overline{L}_c = \frac{0{,}89\lambda}{2(\sin\Theta_2 - \sin\Theta_1)}$$

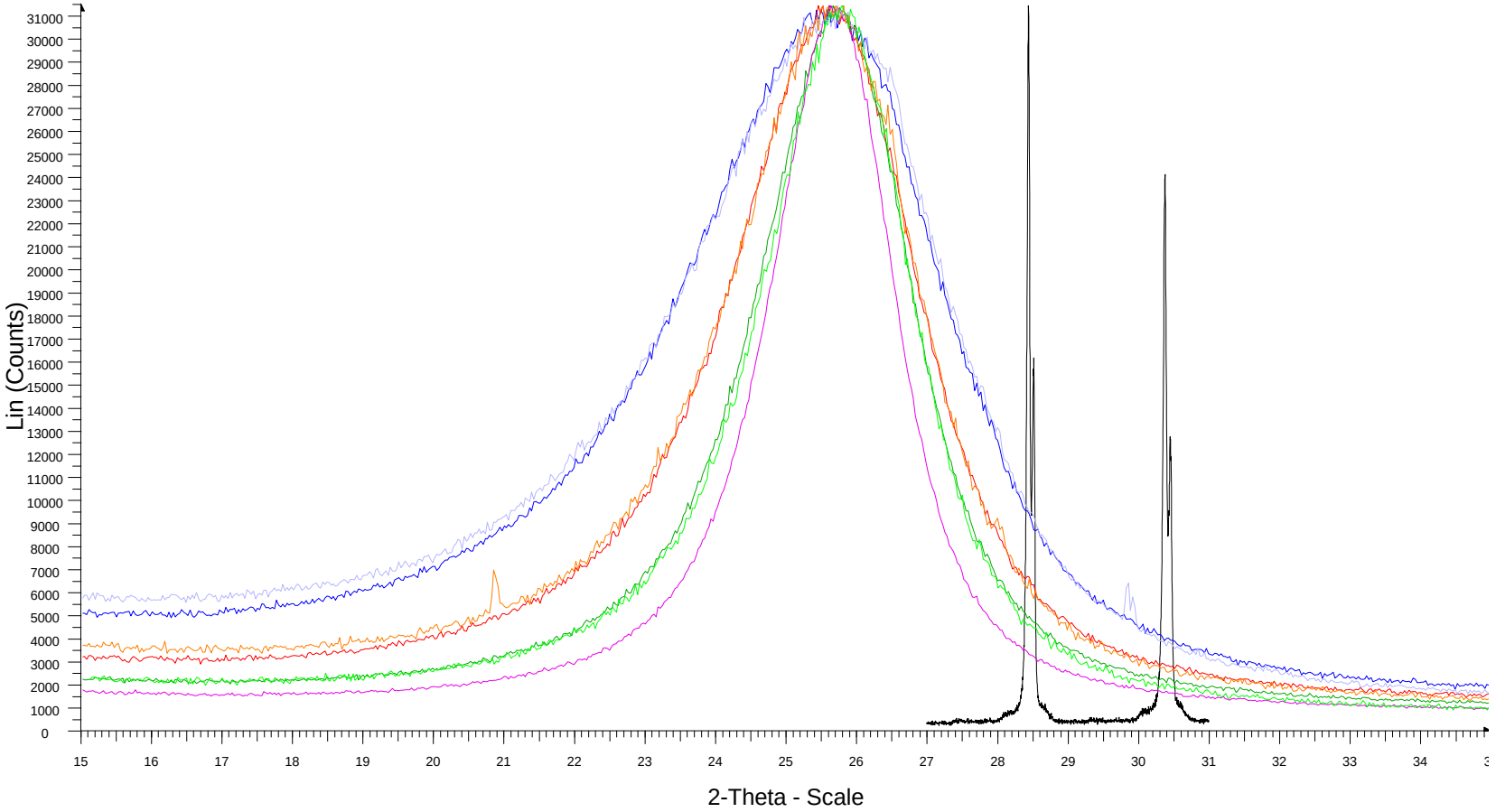
- "The above equations make the assumption that the true line width is equal to the measured width, the contribution of instrumental line broadening is negligible."
  - This assumption is only valid for very low crystalline carbon !

ISO 17499

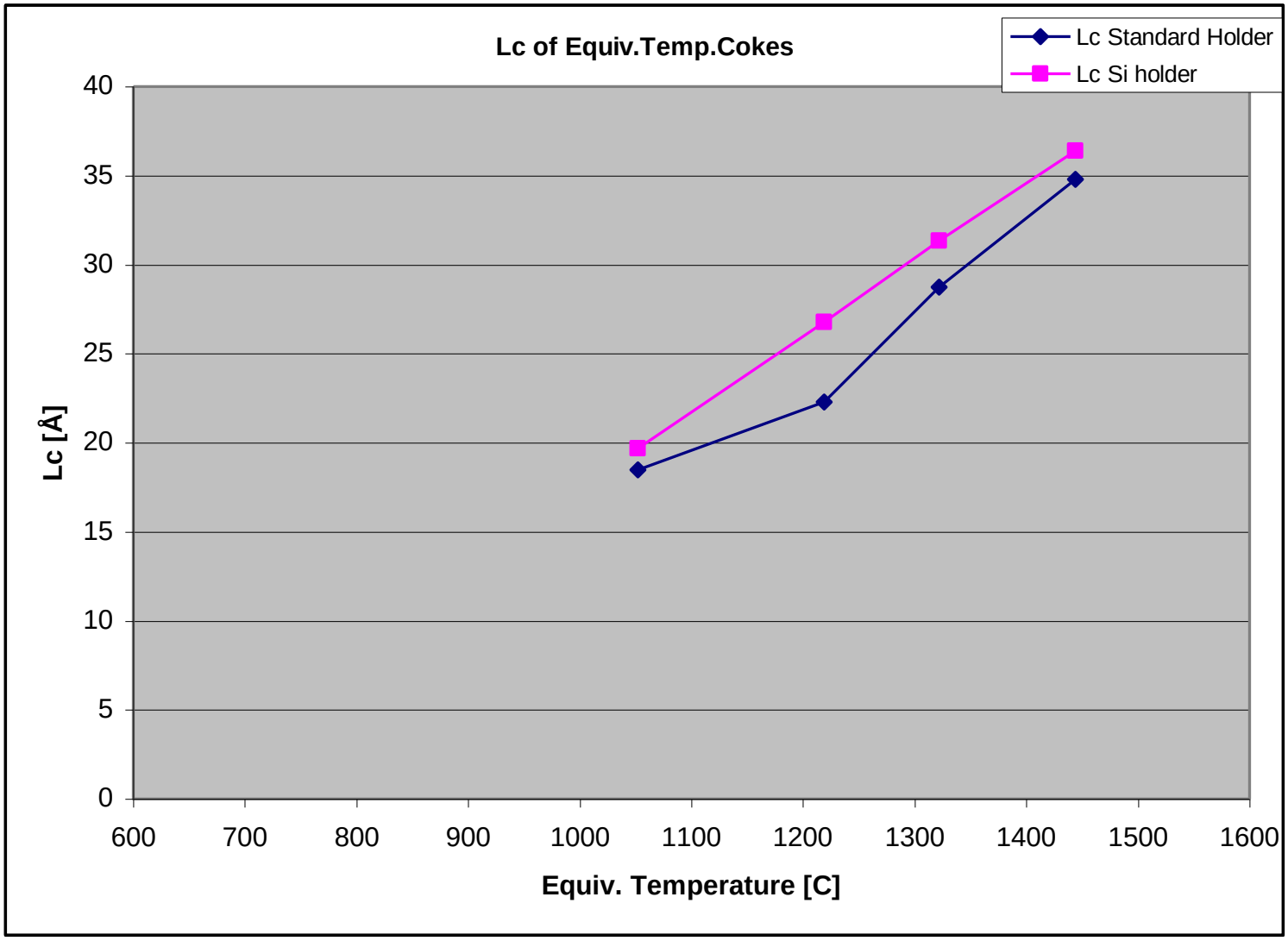
- Carbonaceous materials used in the production of aluminium — Determination of baking level expressed by equivalent temperature
  - used to quantify heat treatment of anodes for aluminium production
- L_c is measured on a set of standard cokes heat-treated to different known temperatures
- A calibration for the L_c vs. equivalent temperature is calculated (for that laboratory)
- This equation is used to determine the equivalent temperature of the heat treated material (there is no way to measure it directly)
- This is a way to get around the problems with L_c measurements

ISO 17499

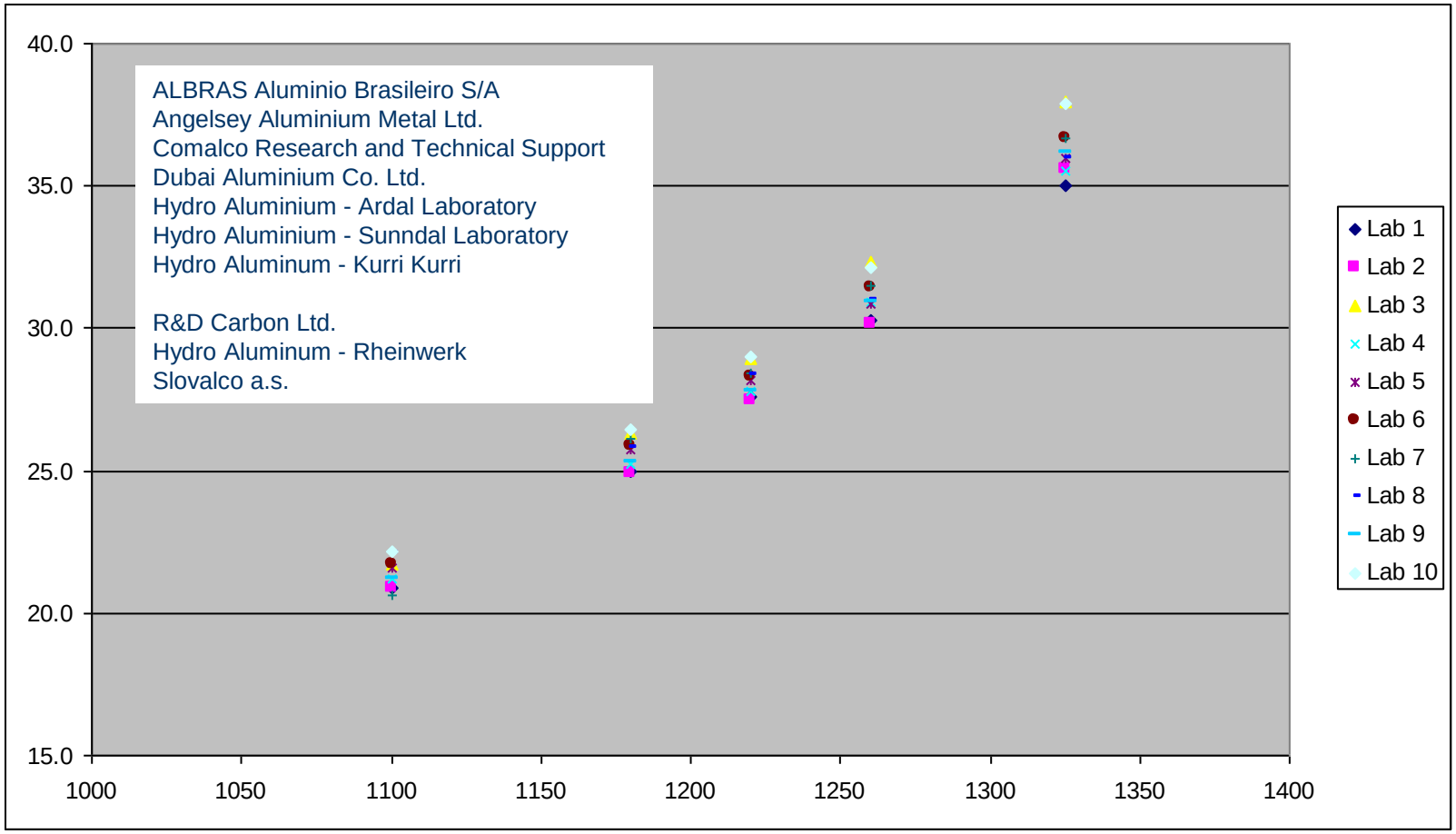
Cokes for Equivalent Temperature Calibration



ISO 17499


Lc of Equiv.Temp.Cokes
Lc Standard Holder
Lc Si holder
Lc [Å]
0
5
10
15
20
25
30
35
40
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
Equiv. Temperature [C]

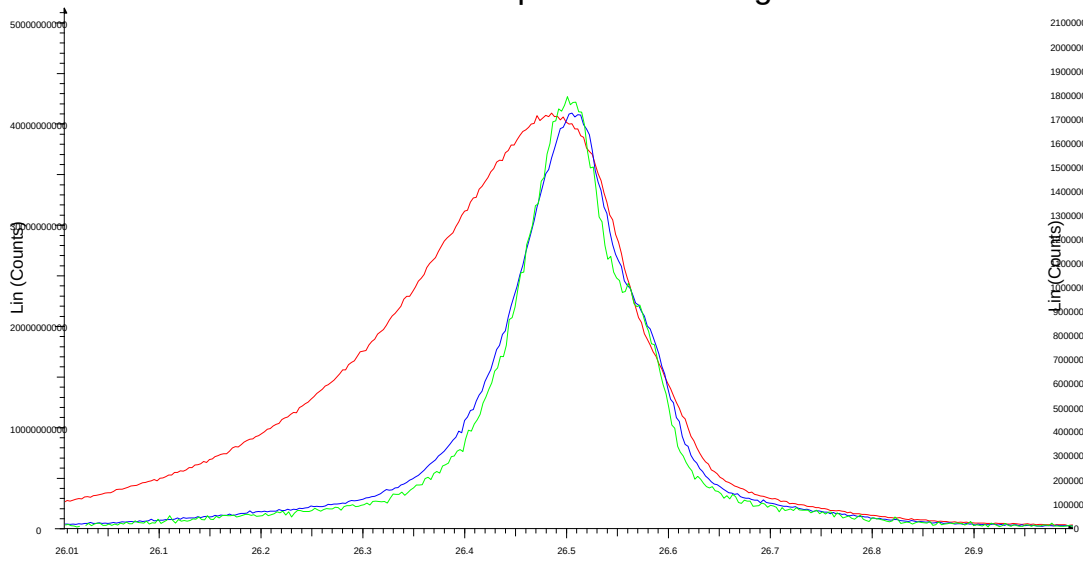
ISO 17499 – Comparison of Labs



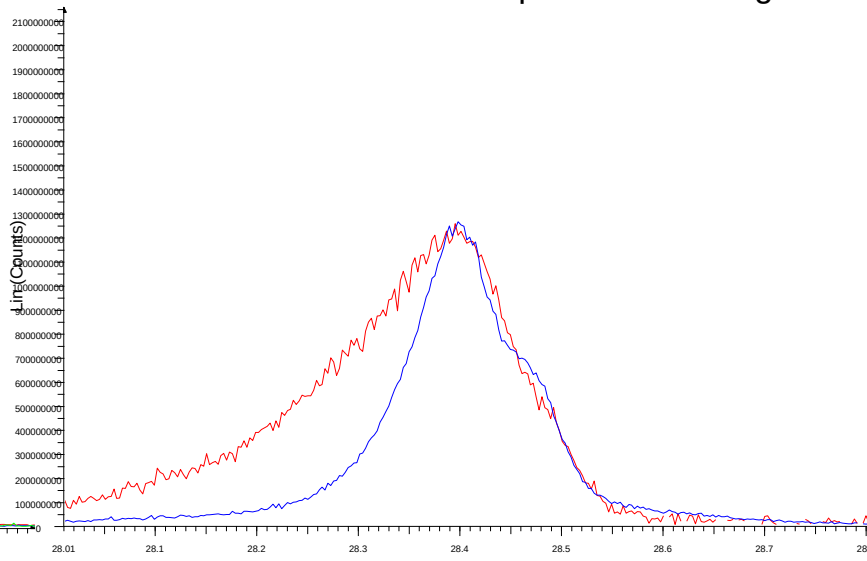
Absorption Effect

- Carbon has very low absorption of X-rays
- X-rays penetrates deep into the sample, causing substantial peak broadening

C Peak Absorption Broadening

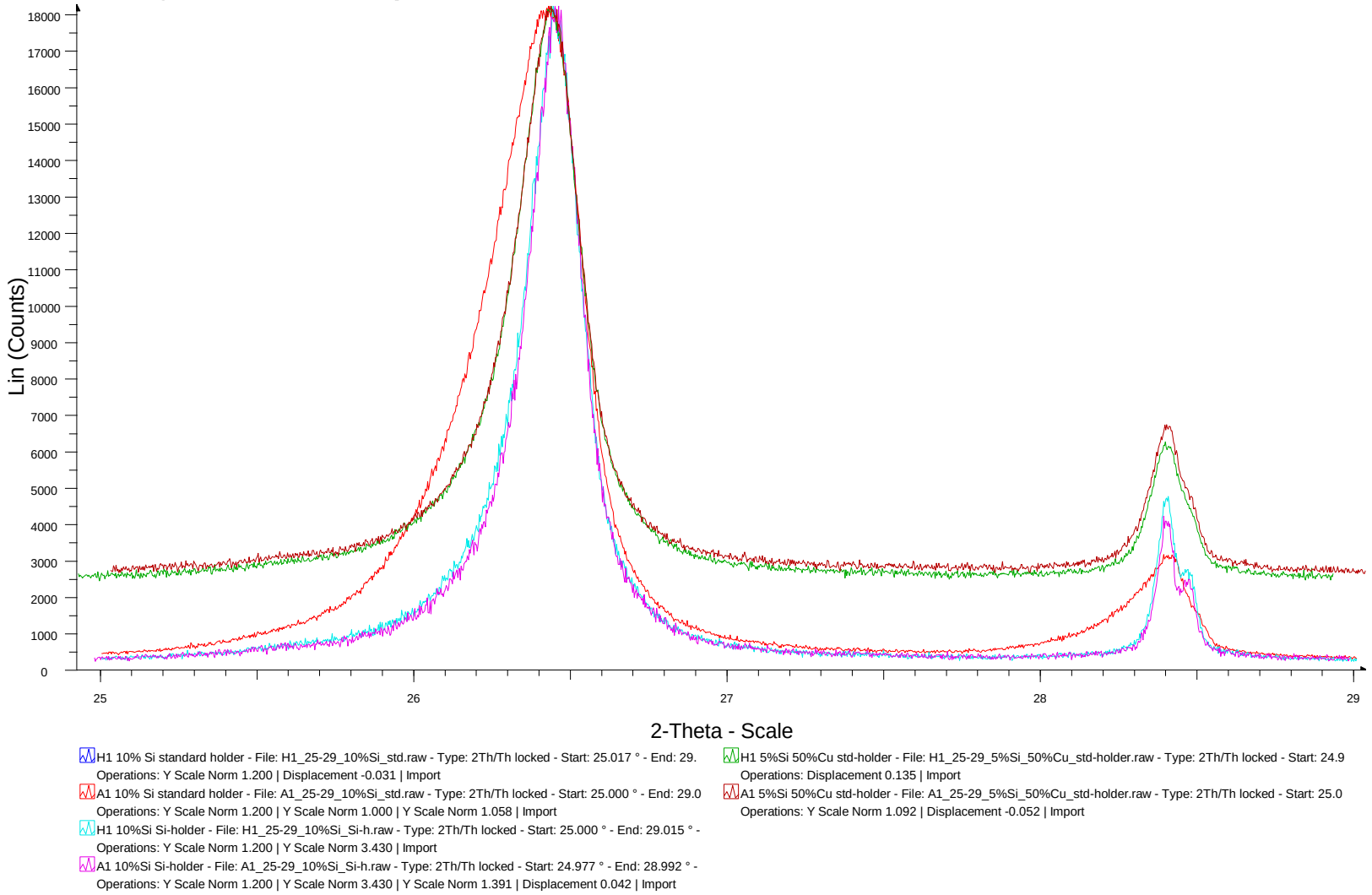


Si Peak Absorption Broadening



Effect of Sample Preparation

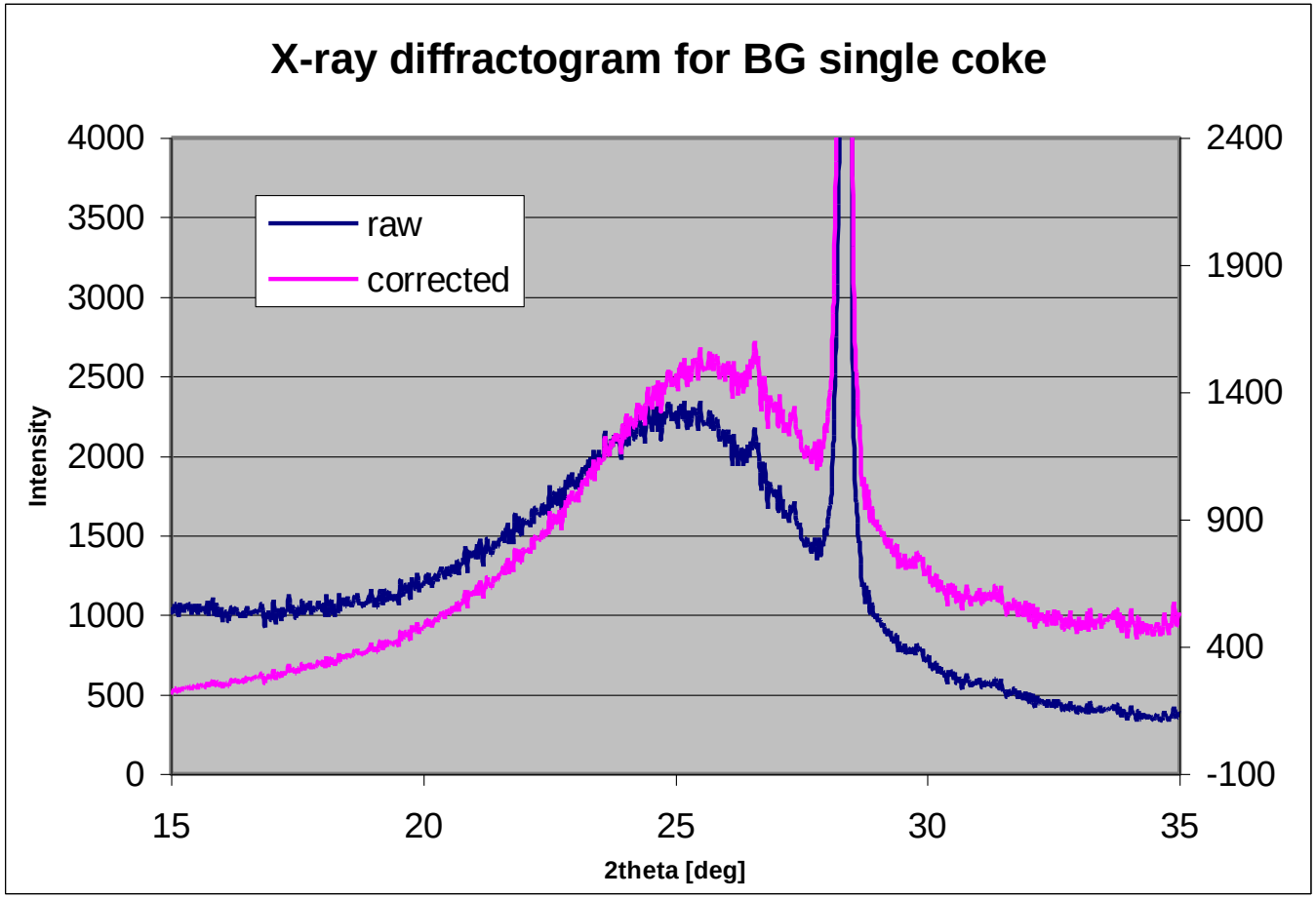
Synthetic Graphites, Std holder / mixed with Cu / Si holder



Iwashita et.al. (2004)

- **Specification for a standard procedure of X-ray diffraction measurements on carbon materials**
- Regarded as ”State of the art” for L_c measurements
- Add silicon as internal reference to peak position
  - Effect is largest for high crystalline carbons
- Correct for angle dependent factors
  - Lorentz factor (L)
  - Polarization factor (P)
  - Absorption factor (A)
  - Atomic Scattering factor (F_c)
  - Effect of corrections is largest for low crystalline carbons

$L \cdot P \cdot A \cdot F_c$ correction on coke



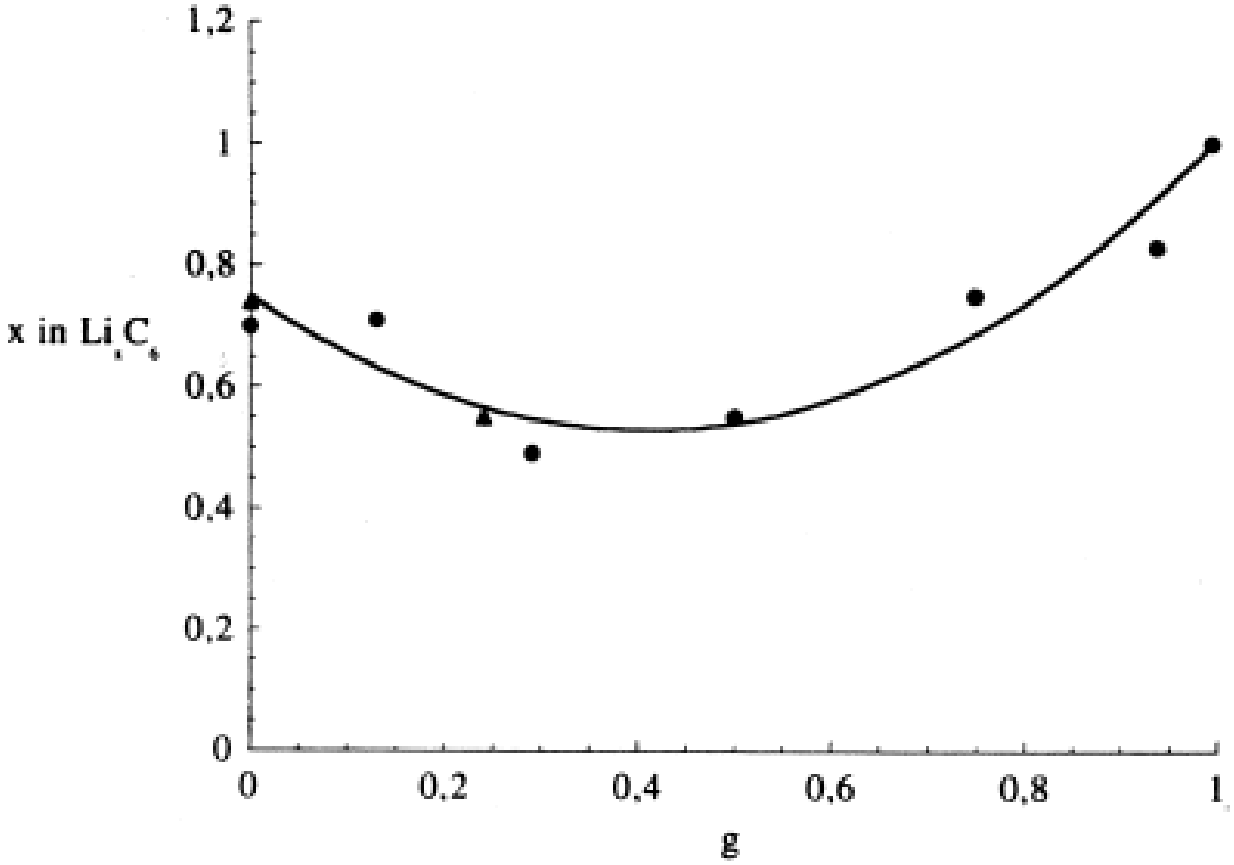
- d_{002} value shifts to lower value for low L_c carbons
- still fails to correct for absorption effect

Relevance to Battery Technology

- Flandrois model (based on Mering):
  - Each graphite layer is either α state or β state
  - β state = perfect graphite
  - α state = interstitial carbon on face of layer
  - Graphitization = cleaning face of each layer from α → β state
  - αα layers: mean interlayer distance d = 3.44 Å
  - ββ layers: mean interlayer distance d = 3.354 Å (graphite)

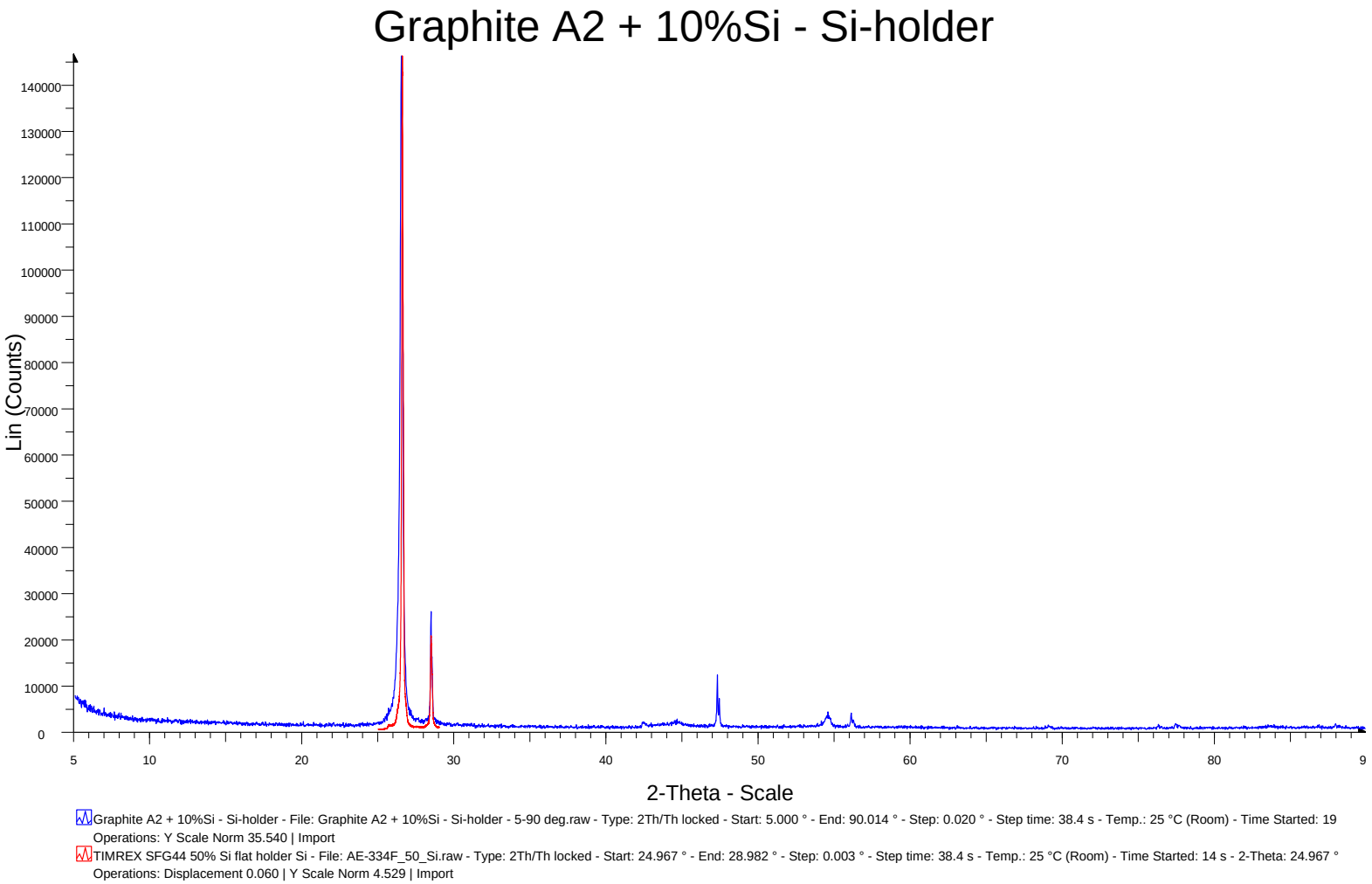
  - g = (3.44 - d) / (3.44 - 3.354)
  - g is the fraction of layers in the β state (graphitic)

Lithium Intercalation in Batteries

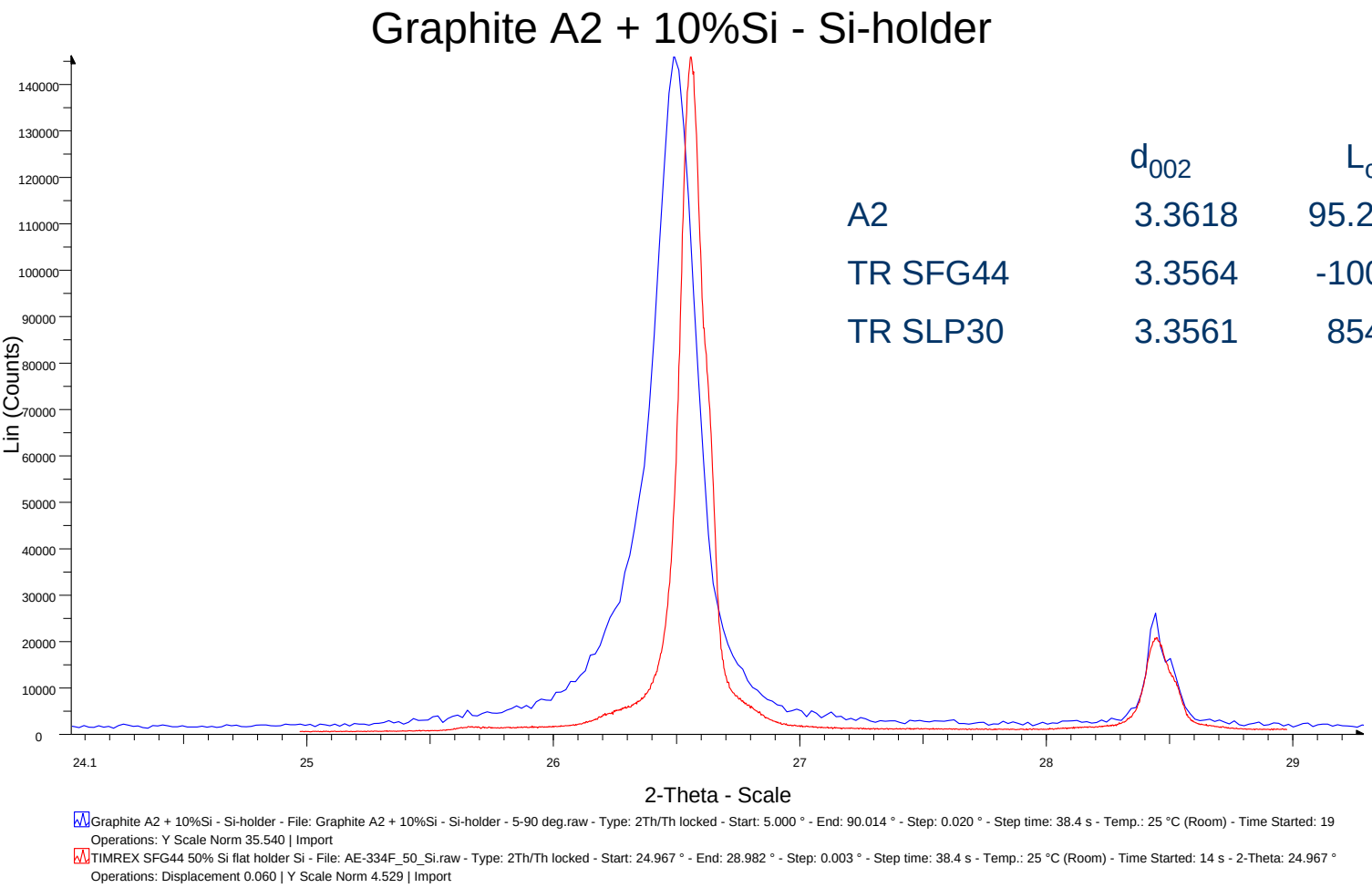


- Relation of x in Li_xC_6 and g in Flandrois/Méring's model

Synthetic Graphite for Battery use



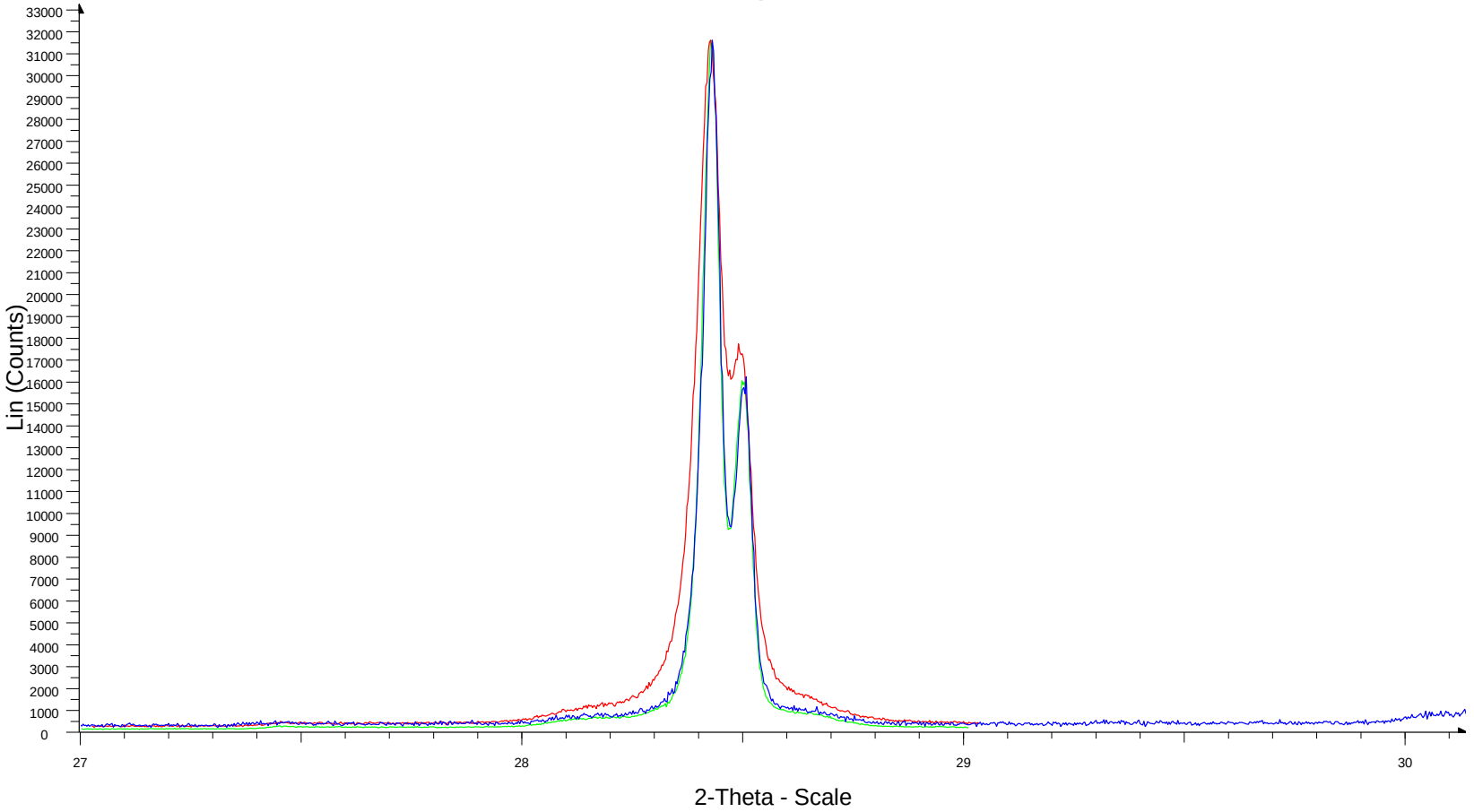
Synthetic Graphite for Battery use



	d_{002}	L_c	L_a
A2	3.3618	95.26451	236.9803
TR SFG44	3.3564	-1005.17	-95.1331
TR SLP30	3.3561	854.133	-175.786

Comparison of Si used as standard

Si standard: Silgrain vs Solar



Mono Wafer + LaB6 - Si-holder - File: Mono Wafer + LaB6 - Si-holder - 27-31 deg.raw - Type: 2Th/Th locked - Start: 26.981 ° - End: 30.996 ° - Step: 0.003 ° - Step time: 38.4 s - Temp.: 25 °C (Room) - Time Started: 13
Operations: Displacement 0.034 | Y Scale Norm 7.254 | Import

Solar Cell Poly - Si-holder - File: Solar Cell Poly - Si-holder - 28-29 deg.raw - Type: 2Th/Th locked - Start: 27.000 ° - End: 29.013 ° - Step: 0.003 ° - Step time: 38.4 s - Temp.: 25 °C (Room) - Time Started: 14 s - 2-Theta
Operations: Import

Silgrain U90 - Si-holder - File: Silgrain U90 - Si-holder - 28-29 deg.raw - Type: 2Th/Th locked - Start: 27.023 ° - End: 29.036 ° - Step: 0.003 ° - Step time: 38.4 s - Temp.: 25 °C (Room) - Time Started: 14 s - 2-Theta: 27.
Operations: Y Scale Norm 2.287 | Displacement -0.042 | Import