

# A Review of Problems With Measurements of $L_c$ in Carbon Materials

Stein Rørvik

SINTEF Materials and Chemistry

Trondheim, Norway

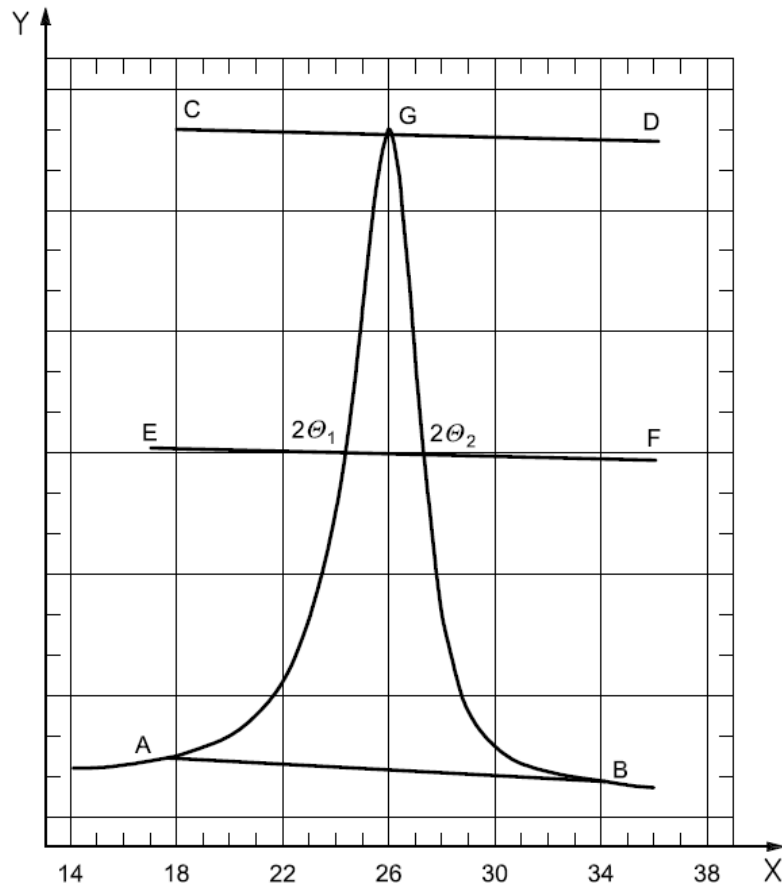
# Why $L_c$ Measurements ?

- 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)

$$\bar{L}_c = \frac{0,89\lambda}{2(\sin\theta_2 - \sin\theta_1)}$$

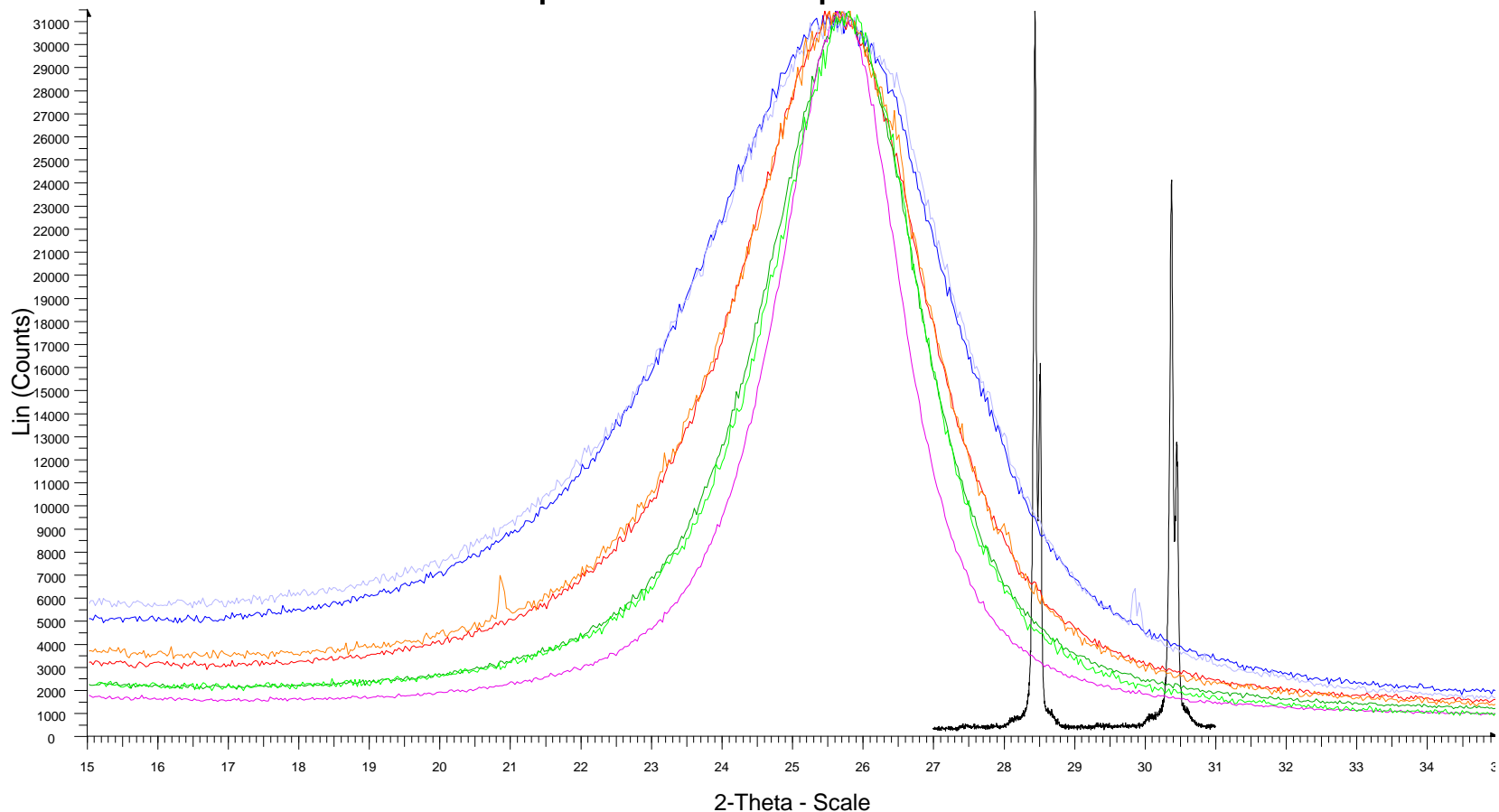
- “The above equations make the assumption that the true line width is equal to the measured width, the contribution of instrumental line broadening is negligible.”
  - This assumption is only valid for very low crystalline carbon !

# 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**

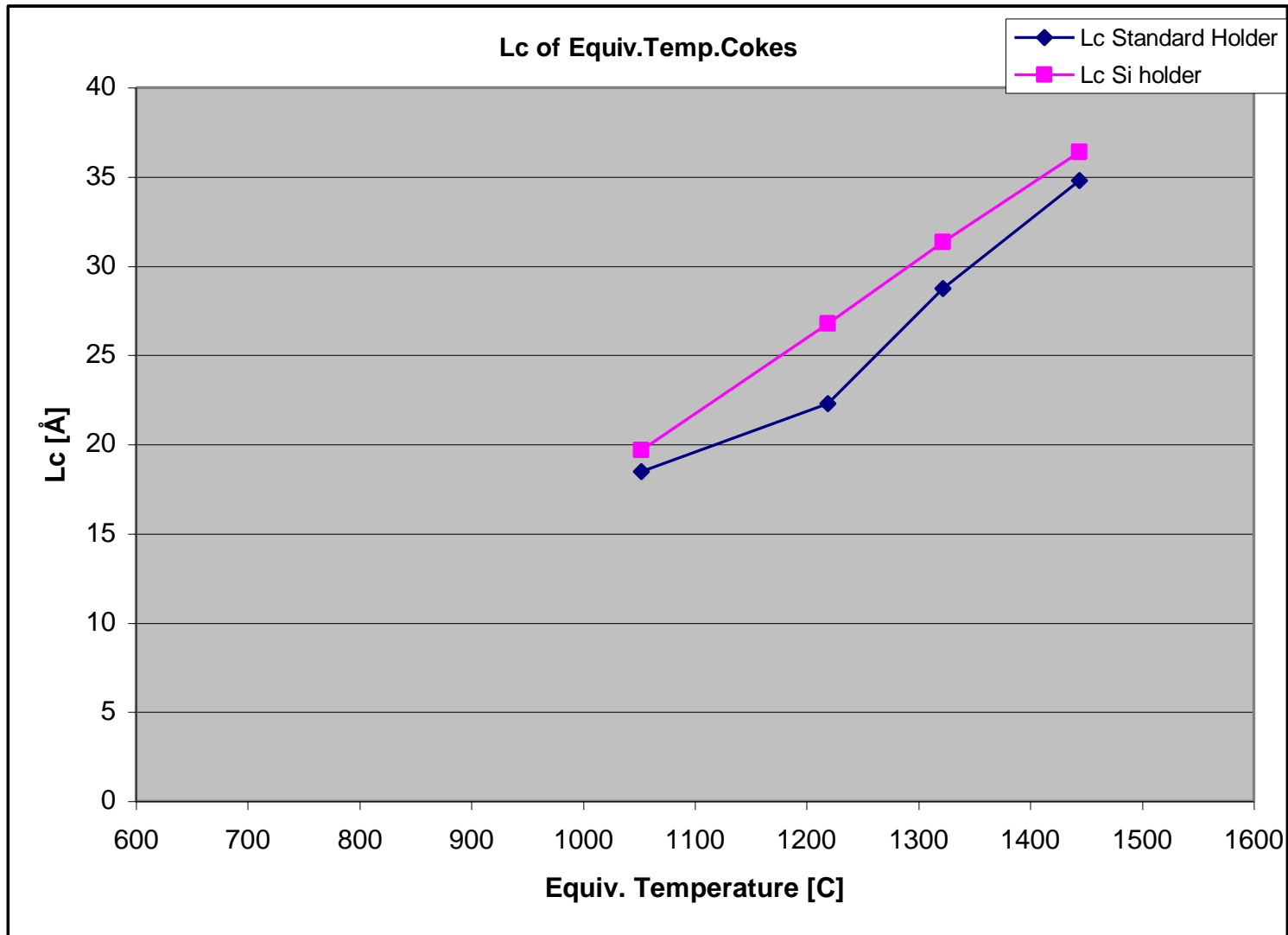
# ISO 17499

## Cokes for Equivalent Temperature Calibration



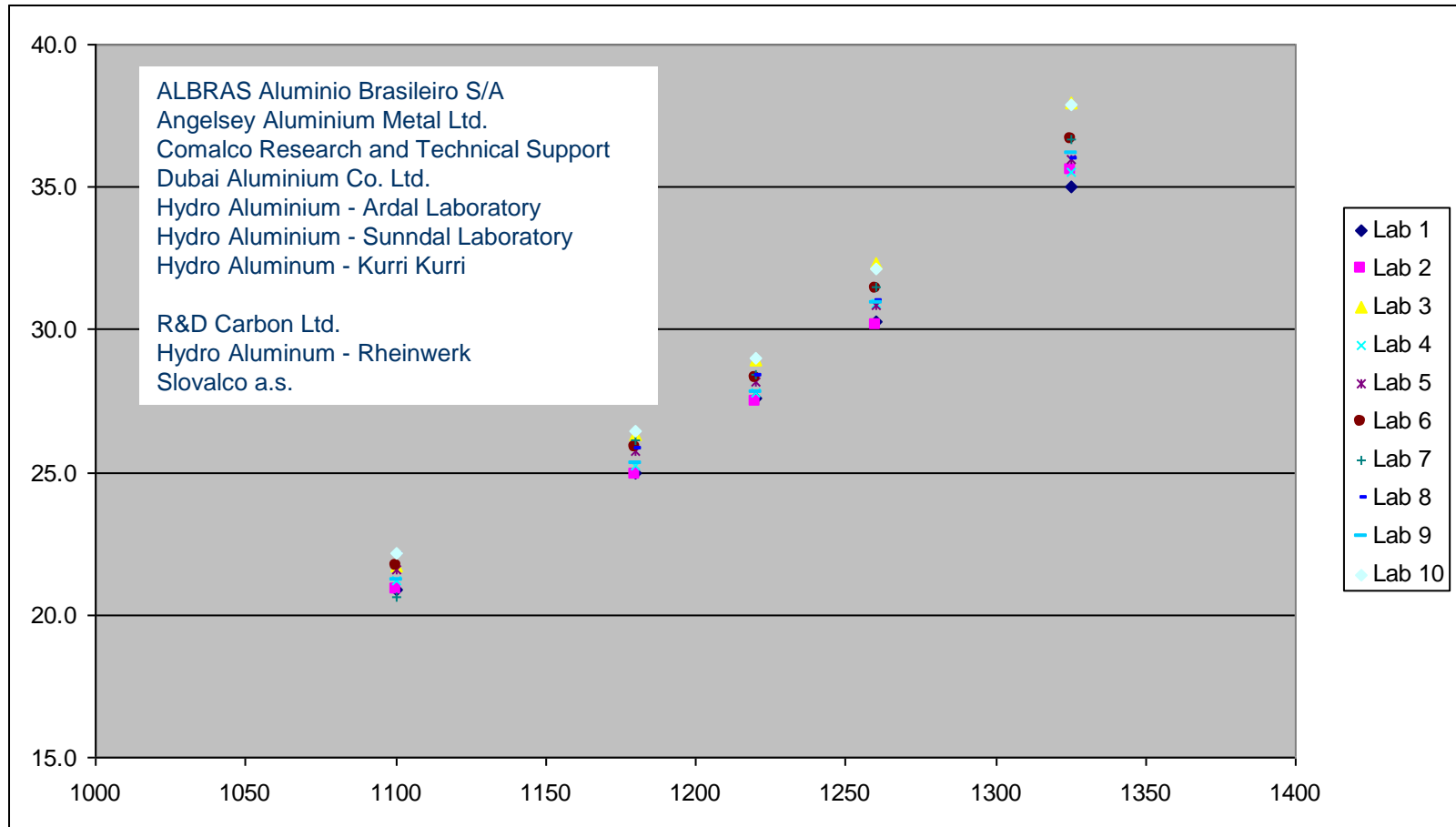
- Mono Wafer + LaB6 - Si-holder - File: Mono Wafer + LaB6 - Si-holder - Operations: Y Scale Norm 1.278 | Y Scale Norm 5.650 | Import
- M1444 standard holder - File: M1444 std holder.raw - Type: 2Th/Th loc Operations: Import
- M1444 Si holder - File: M1444 Si holder.raw - Type: 2Th/Th locked - St Operations: Y Scale Norm 5.731 | Import
- M1052 standard holder - File: M1052 std holder.raw - Type: 2Th/Th loc Operations: Y Scale Norm 1.278 | Y Scale Norm 1.265 | Y Scale Norm
- M1052 Si holder - File: M1052 Si holder.raw - Type: 2Th/Th locked - St Operations: Y Scale Norm 1.965 | Import
- M1219 standard holder - File: M1219 std holder.raw - Type: 2Th/Th loc Operations: Y Scale Norm 1.278 | Y Scale Norm 1.265 | Import
- M1219 Si holder - File: M1219 Si holder.raw - Type: 2Th/Th locked - St Operations: Y Scale Norm 3.376 | Import
- M1322 standard holder - File: M1322 std holder.raw - Type: 2Th/Th loc Operations: Y Scale Norm 1.278 | Import
- M1322 Si holder - File: M1322 Si holder.raw - Type: 2Th/Th locked - St Operations: Displacement -0.173 | Y Scale Norm 3.636 | Import

# ISO 17499





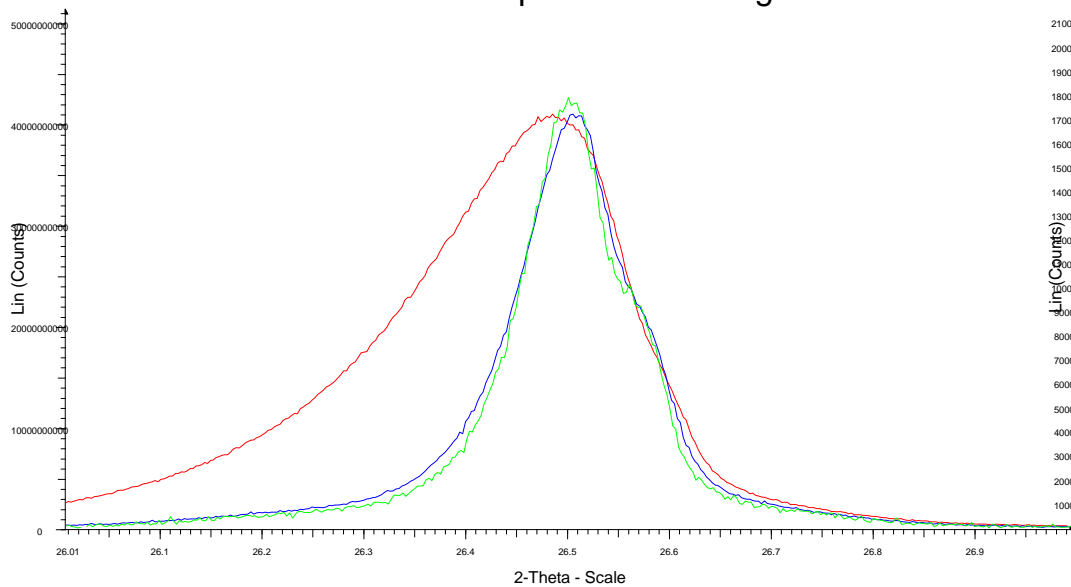
# ISO 17499 – Comparison of Labs



# Absorption Effect

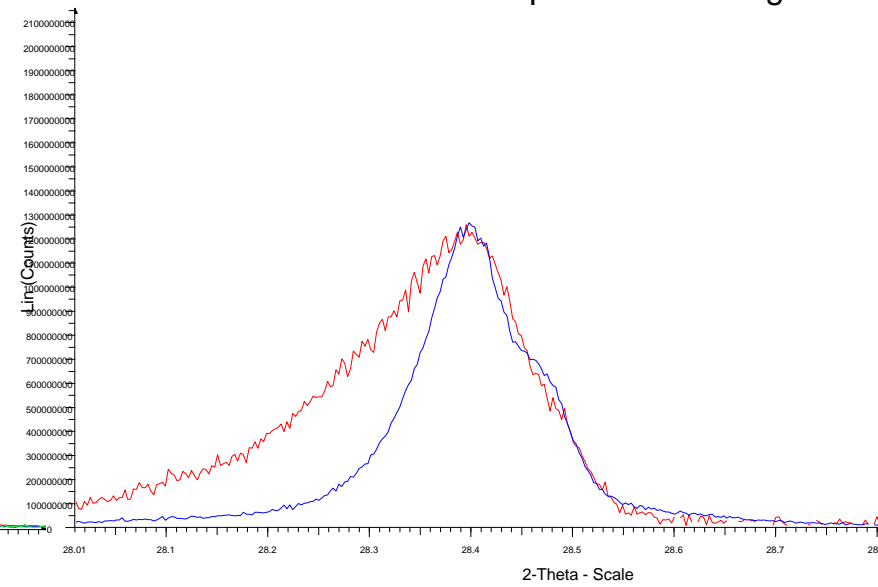
- Carbon has very low absorption of X-rays
- X-rays penetrates deep into the sample, causing substantial peak broadening

C Peak Absorption Broadening



AE-158 10% Si standard holder - File: AE-158\_10.raw - Type: 2Th/Th locked - Start: 25.000 ° - End: 29.015 ° - Step: 0.003 ° - Step time: 38.4 s - Temp.: 25 °C (Room) - Time Started: 14 s - 2-Theta: 25.000 ° - Theta: 12.500 ° - Ch Operations: Y Scale Mul 3.750 | Y Scale Mul 60.000 | Y Scale Mul 35.417 | Y Scale Norm 1.752 | Background 100.000,1.000 | Y Scale Mul 4  
AE-158 50% Si standard holder - File: AE-158\_50.raw - Type: 2Th/Th locked - Start: 25.000 ° - End: 29.015 ° - Step: 0.003 ° - Step time: 38.4 s - Temp.: 25 °C (Room) - Time Started: 14 s - 2-Theta: 25.000 ° - Theta: 12.500 ° - Ch Operations: Y Scale Norm 10.871 | Y Scale Mul 3.833 | Y Scale Mul 5.400 | Y Scale Norm 11.333 | Y Scale Mul 3.125 | Y Scale Norm 1.747 |  
AE-158 90% Si standard holder - File: AE-158\_90.raw - Type: 2Th/Th locked - Start: 24.981 ° - End: 28.996 ° - Step: 0.003 ° - Step time: 38.4 s - Temp.: 25 °C (Room) - Time Started: 13 s - 2-Theta: 24.981 ° - Theta: 12.500 ° - Ch Operations: Y Scale Mul 1.833 | Y Scale Norm 32.453 | Y Scale Mul 3.917 | Displacement 0.034 | Y Scale Mul 1.770 | Y Scale Norm 35.417 |

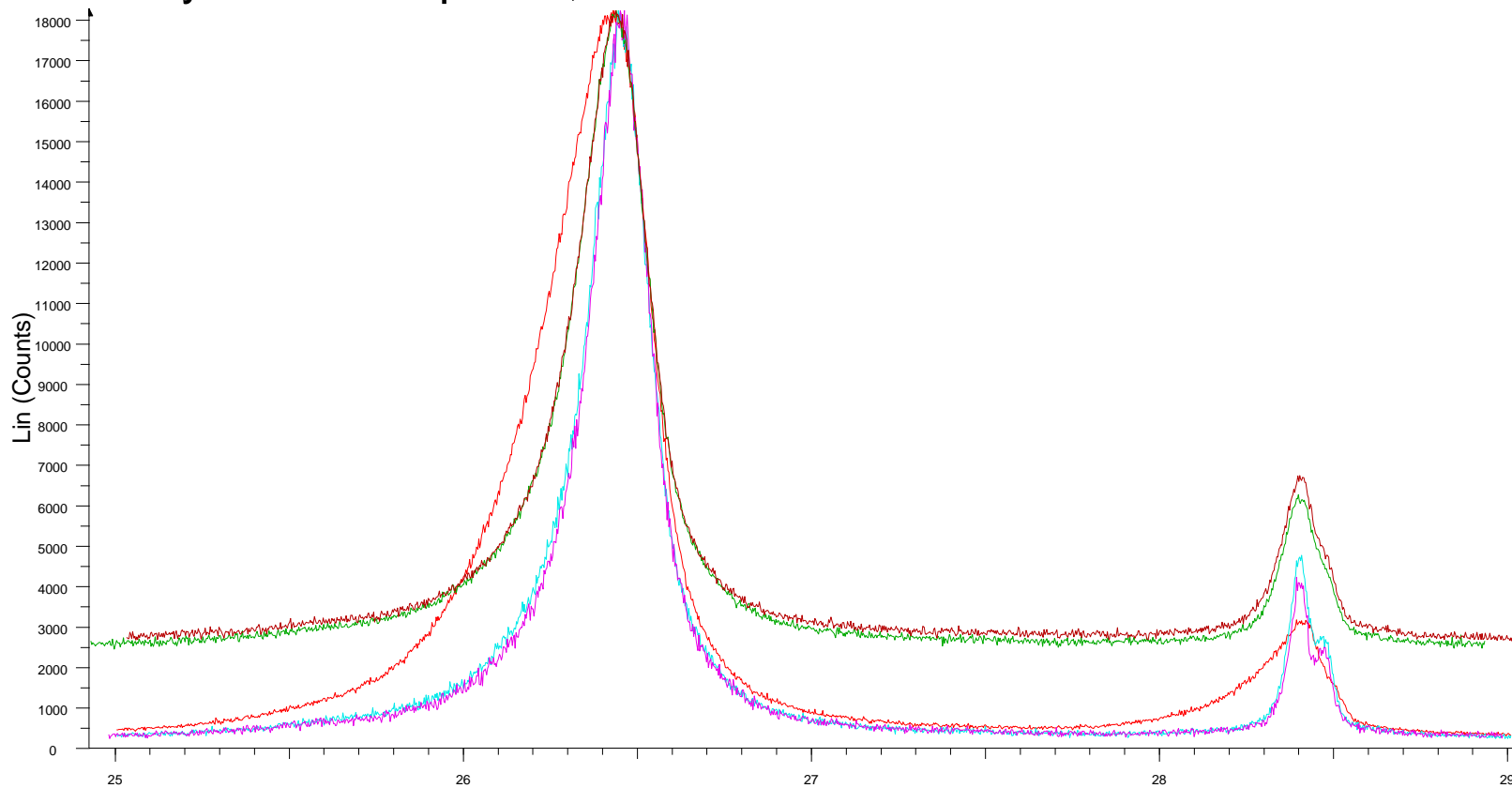
Si Peak Absorption Broadening



AE-158 10% Si standard holder - File: AE-158\_10.raw - Type: 2Th/Th locked - Start: 25.000 ° - End: 29.015 ° - Step: 0.003 ° - Step time: 38.4 s - Temp.: 25 °C (Room) - Time Started: 14 s - 2-Theta: 25.000 ° - Theta: 12.500 ° - Ch Operations: Y Scale Mul 3.750 | Y Scale Mul 60.000 | Y Scale Mul 35.417 | Y Scale Norm 1.752 | Background 100.000,1.000 | Y Scale Mul 4  
AE-158 50% Si standard holder - File: AE-158\_50.raw - Type: 2Th/Th locked - Start: 25.000 ° - End: 29.015 ° - Step: 0.003 ° - Step time: 38.4 s - Temp.: 25 °C (Room) - Time Started: 14 s - 2-Theta: 25.000 ° - Theta: 12.500 ° - Ch Operations: Y Scale Mul 3.833 | Y Scale Mul 5.400 | Y Scale Norm 11.333 | Y Scale Mul 3.125 | Y Scale Norm 1.747 | Background 100.000,1.000 |  
AE-158 90% Si standard holder - File: AE-158\_90.raw - Type: 2Th/Th locked - Start: 24.981 ° - End: 28.996 ° - Step: 0.003 ° - Step time: 38.4 s - Temp.: 25 °C (Room) - Time Started: 13 s - 2-Theta: 24.981 ° - Theta: 12.500 ° - Ch Operations: Y Scale Mul 3.917 | Displacement 0.034 | Y Scale Mul 1.770 | Y Scale Norm 35.417 | Y Scale Mul 1.750 | Background 100.000,1.000 |

# Effect of Sample Preparation

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



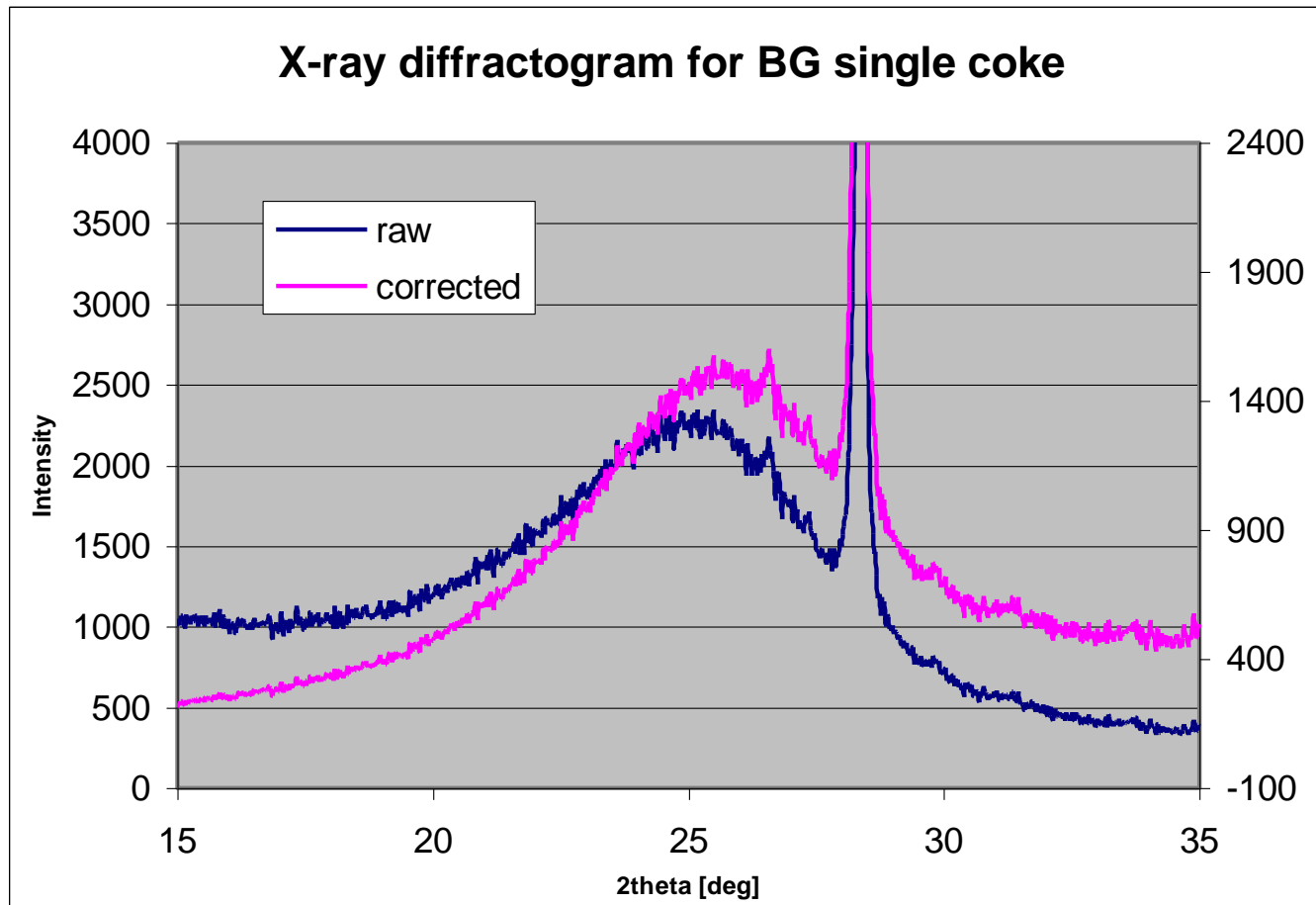
2-Theta - Scale

- H1 10% Si standard holder - File: H1\_25-29\_10%Si\_std.raw - Type: 2Th/Th locked - Start: 25.017 ° - End: 29.0  
Operations: Y Scale Norm 1.200 | Displacement -0.031 | Import
- A1 10% Si standard holder - File: A1\_25-29\_10%Si\_std.raw - Type: 2Th/Th locked - Start: 25.000 ° - End: 29.0  
Operations: Y Scale Norm 1.200 | Y Scale Norm 1.000 | Y Scale Norm 1.058 | Import
- H1 10%Si Si-holder - File: H1\_25-29\_10%Si\_Si-h.raw - Type: 2Th/Th locked - Start: 25.000 ° - End: 29.015 ° -  
Operations: Y Scale Norm 1.200 | Y Scale Norm 3.430 | Import
- A1 10%Si Si-holder - File: A1\_25-29\_10%Si\_Si-h.raw - Type: 2Th/Th locked - Start: 24.977 ° - End: 28.992 ° -  
Operations: Y Scale Norm 1.200 | Y Scale Norm 3.430 | Y Scale Norm 1.391 | Displacement 0.042 | Import
- H1 5%Si 50%Cu std-holder - File: H1\_25-29\_5%Si\_50%Cu\_std-holder.raw - Type: 2Th/Th locked - Start: 24.9  
Operations: Displacement 0.135 | Import
- A1 5%Si 50%Cu std-holder - File: A1\_25-29\_5%Si\_50%Cu\_std-holder.raw - Type: 2Th/Th locked - Start: 25.0  
Operations: Y Scale Norm 1.092 | Displacement -0.052 | Import

# 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·P·A·F<sub>c</sub> correction on coke

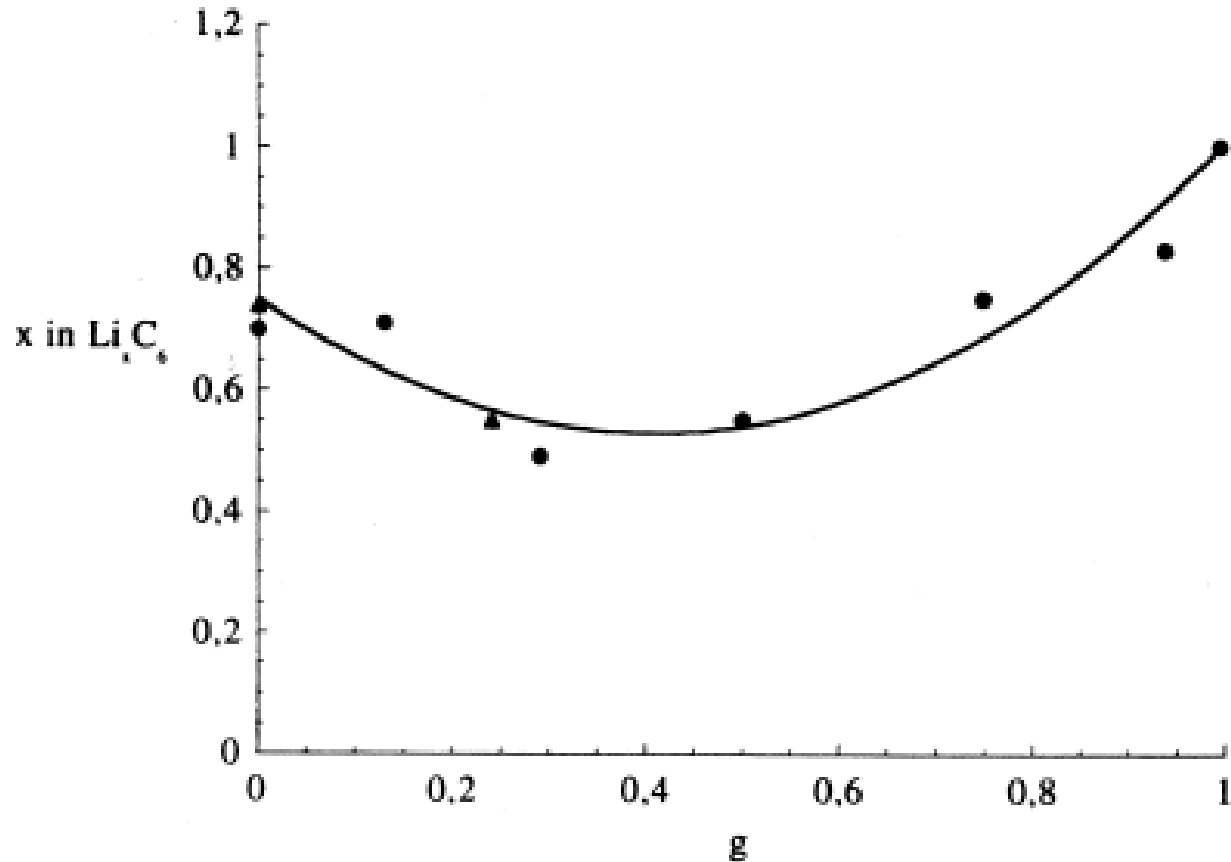


- $d_{002}$  value shifts to lower value for low  $L_c$  carbons
- still fails to correct for absorption effect

# Relevance to Battery Technology

- Flandrois model (based on Mering):
  - Each graphite layer is either  $\alpha$  state or  $\beta$  state
  - $\beta$  state = perfect graphite
  - $\alpha$  state = interstitial carbon on face of layer
  - Graphitization = cleaning face of each layer from  $\alpha \rightarrow \beta$  state
  - $\alpha\alpha$  layers: mean interlayer distance  $d = 3.44 \text{ \AA}$
  - $\beta\beta$  layers: mean interlayer distance  $d = 3.354 \text{ \AA}$  (graphite)
  
  - $g = (3.44 - d) / (3.44 - 3.354)$
  - $g$  is the fraction of layers in the  $\beta$  state (graphitic)

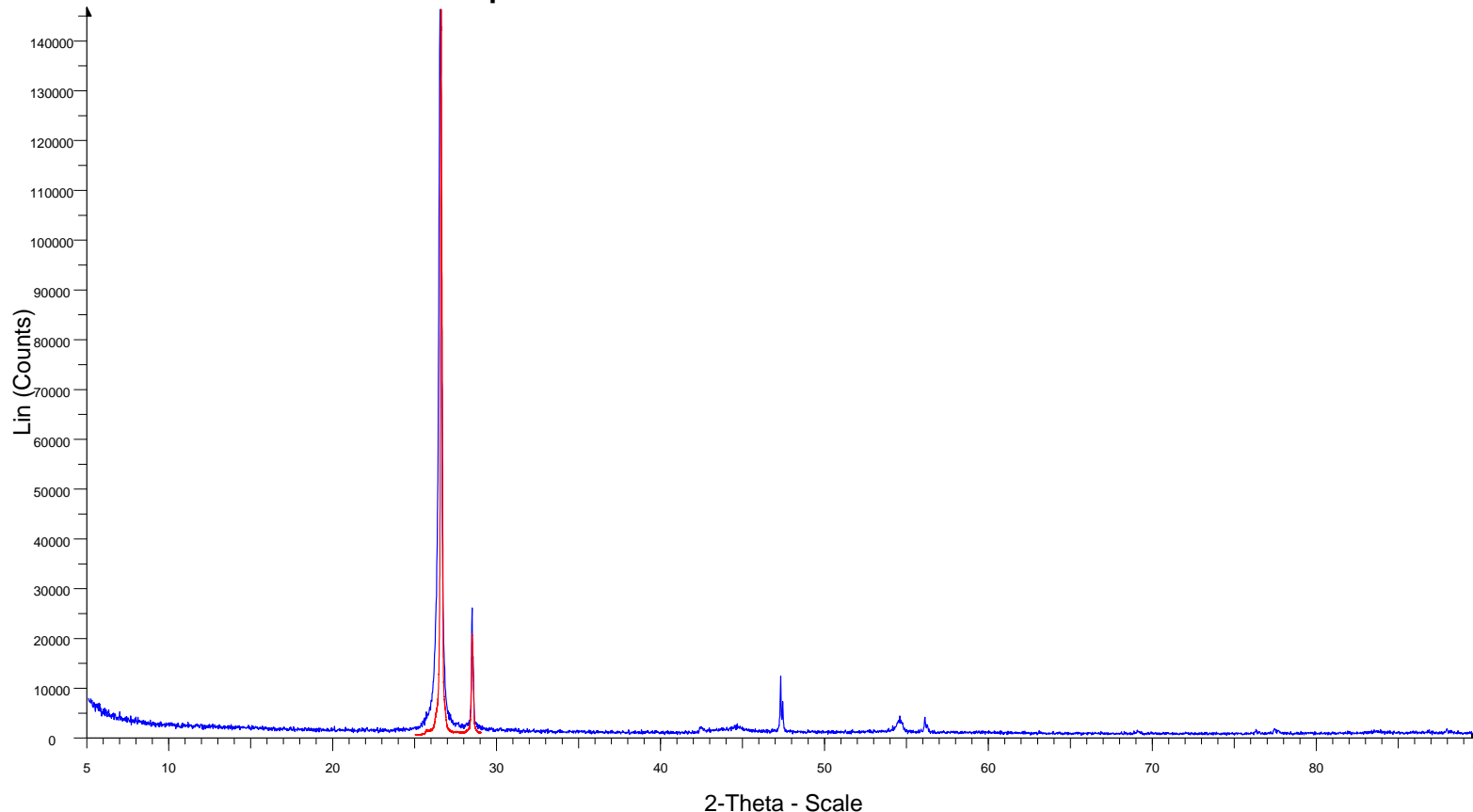
# Lithium Intercalation in Batteries



- Relation of  $x$  in  $\text{Li}_x\text{C}_6$  and  $g$  in Flandrois/Méring's model

# Synthetic Graphite for Battery use

Graphite A2 + 10%Si - Si-holder



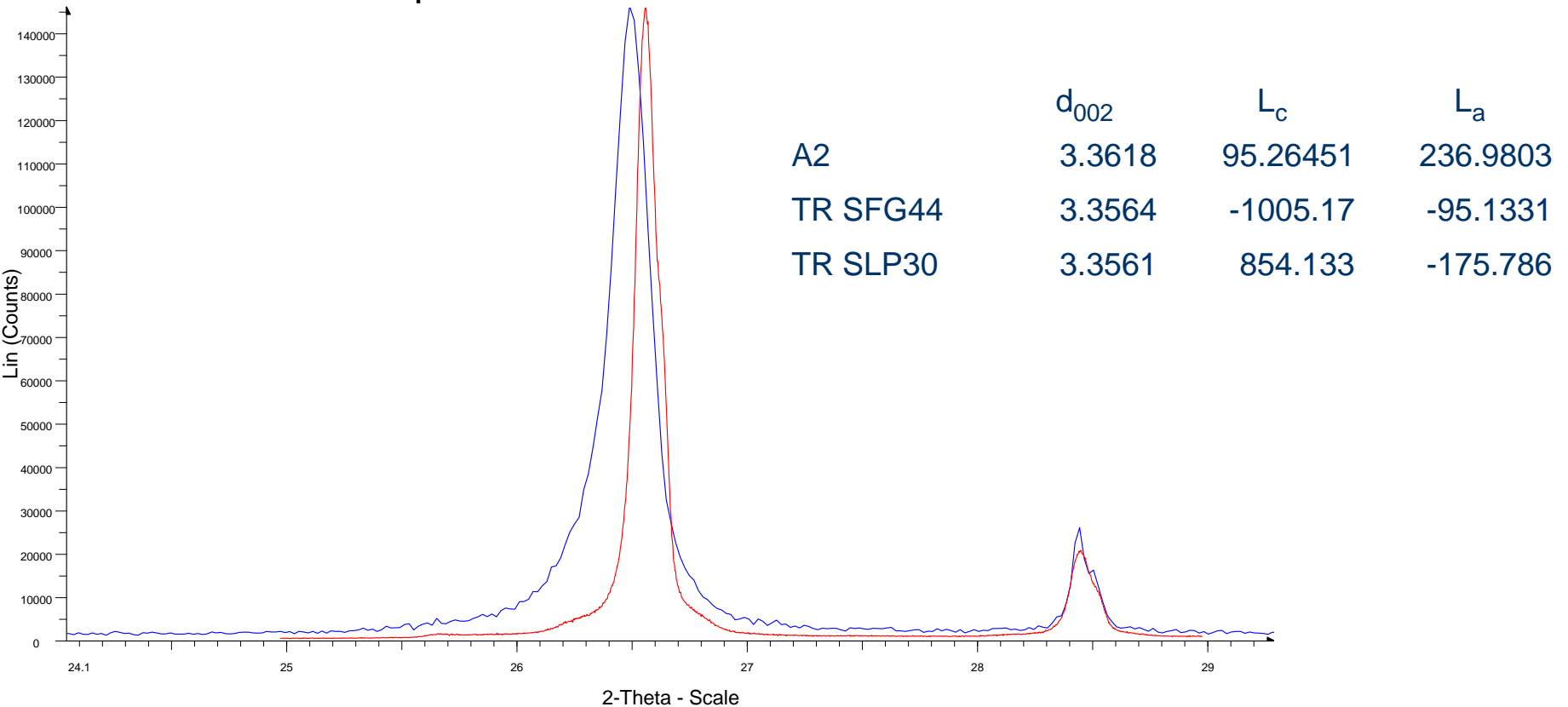
Graphite A2 + 10%Si - Si-holder - File: Graphite A2 + 10%Si - Si-holder - 5-90 deg.raw - Type: 2Th/Th locked - Start: 5.000 ° - End: 90.014 ° - Step: 0.020 ° - Step time: 38.4 s - Temp.: 25 °C (Room) - Time Started: 19  
Operations: Y Scale Norm 35.540 | Import

TIMREX SFG44 50% Si flat holder Si - File: AE-334F\_50\_Si.raw - Type: 2Th/Th locked - Start: 24.967 ° - End: 28.982 ° - Step: 0.003 ° - Step time: 38.4 s - Temp.: 25 °C (Room) - Time Started: 14 s - 2-Theta: 24.967 °  
Operations: Displacement 0.060 | Y Scale Norm 4.529 | Import



# Synthetic Graphite for Battery use

Graphite A2 + 10%Si - Si-holder

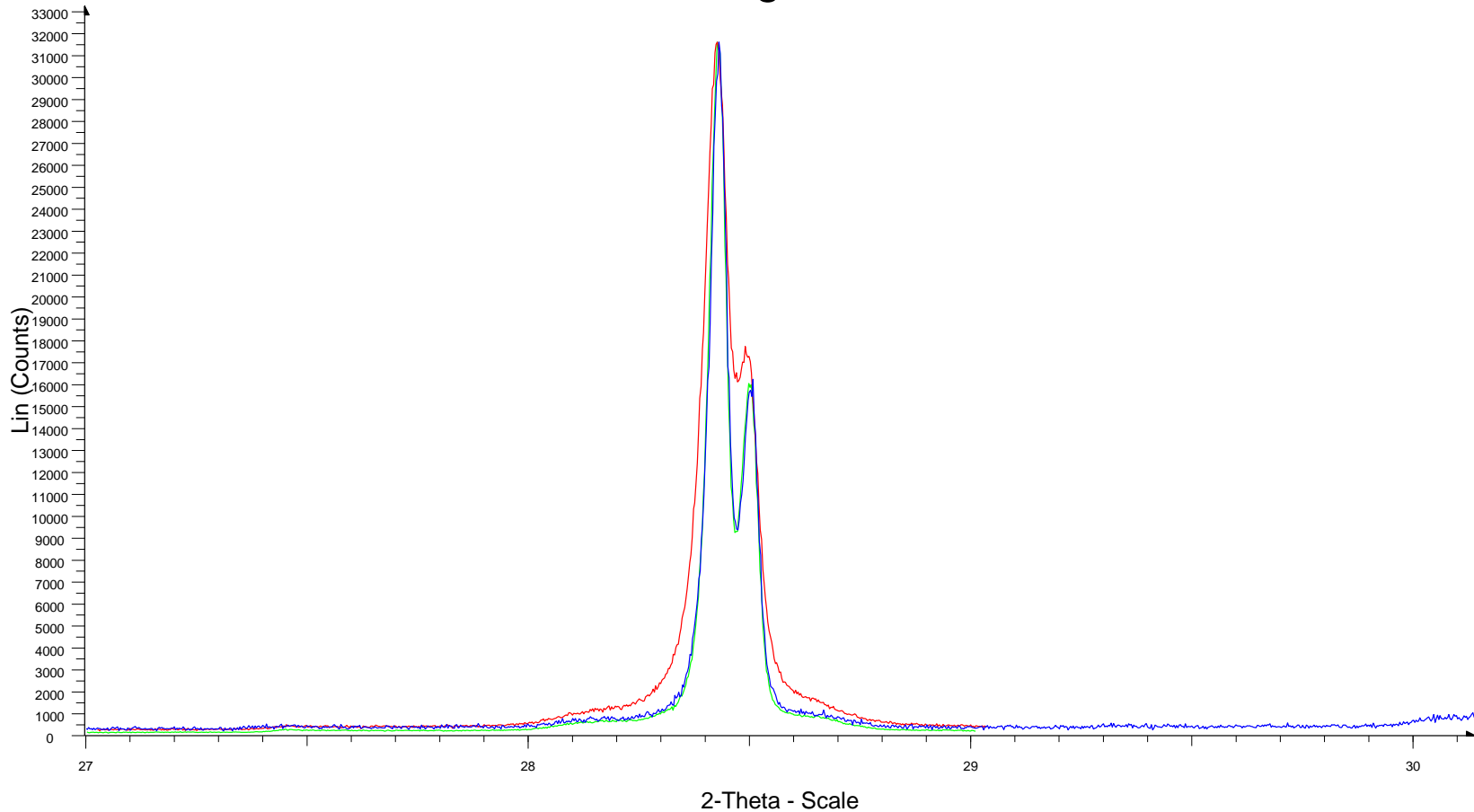


■ Graphite A2 + 10%Si - Si-holder - File: Graphite A2 + 10%Si - Si-holder - 5-90 deg.raw - Type: 2Th/Th locked - Start: 5.000 ° - End: 90.014 ° - Step: 0.020 ° - Step time: 38.4 s - Temp.: 25 °C (Room) - Time Started: 19  
 Operations: Y Scale Norm 35.540 | Import

■ TIMREX SFG44 50% Si flat holder Si - File: AE-334F\_50\_Si.raw - Type: 2Th/Th locked - Start: 24.967 ° - End: 28.982 ° - Step: 0.003 ° - Step time: 38.4 s - Temp.: 25 °C (Room) - Time Started: 14 s - 2-Theta: 24.967 °  
 Operations: Displacement 0.060 | Y Scale Norm 4.529 | Import

# 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