Characterizing Battery Materials with PSA and Raman Spectroscopy

AN264

Characterizing Battery Materials by Particle Size and Shape Analysis and Raman Spectroscopy

Introduction

As the requirements for electric vehicles and other portable devices become more and more demanding, the need for higher performance batteries and the ability to monitor the battery material's physical and chemical characteristics will continue to increase. Of the novel battery materials finding more usage in rechargeable lithium-ion batteries are lithium iron phosphates (LFPs), used to comprise the cathode, and carbon-coated silicon (Si@C), used to make the anode. LFP is of interest because of higher safety, lower cost, and longer cycle life compared to nickel cobalt-based batteries, but on their own have poor electrical conductivity, so it is coated with carbon to improve its conductivity. Carbon-coated silicon is of interest as a potential anode material as silicon has ten times the theoretical capacity of the typical graphite anode, while the carbon coating helps to provide structural stability and improves its conductivity.

Particle size is an important parameter to monitor as it affects nearly all performance parameters for battery materials, but in general smaller and narrow distributions are better than wider and coarser distributions. Smaller particle sizes in general lead to increased surface area availability for electrochemical reactions, but nanosized material can lead to poor packing density and lower volumetric energy density. The other issue with nanosized particles is that it has too high of a surface area, leading to a large lithium loss during the first charge-discharge cycle due to the large surface area of the electrode needing to be passivated. On the other hand, the existence of stray coarse particles can cause lithium plating on the surface of the anode, lowering the capacity and raising the possibility of dendrite formation and short circuiting.

Particle shape is another parameter that can impact the packing density and by extension the volumetric energy density. Irregularly shaped particles have a higher surface area compared to spherical particles of the same size, which increases the area for electrochemical reactions but also leads to a larger lithium loss during the first charge-discharge cycle.

The Partica LA-960V2 Laser Scattering Particle Size Distribution Analyzer with LY-9610 Imaging Unit Accessory.

Raman spectroscopy can be used to gain further chemical information of the carbon for both the carbon coating of LFPs and the carbon-coated silicon particles. The resulting Raman spectra display a G band, the primary mode for graphite, whose width can be used to measure the degree of graphitization, or how well the carbon resembles ideal graphite. Raman spectroscopy can also be used to measure the level of defects through the area integrated intensity ratio of the D band to the G band (A_D/A_G). The degree of graphitization is an important parameter to track for battery performance as high degrees of graphitization leads to increased electrical conductivity and lithium ion intercalation efficiency, while the level of defects of graphite is important to track as a moderate level of defects helps to improve capacity rates but too many defects can impact the structural quality of the graphite.

Two LFP powder samples, one in an agglomerated state before processing (LFP-1) and another in an un-agglomerated state after processing (LFP-2), and one carbon-coated silicon powder sample were provided for probing the physical properties by particle size and shape analysis and for probing the chemical properties by Raman spectroscopy to identify potential parameters that would impact battery performance.

Analytical Test Method for Particle Characterization Analysis

Particle size distribution was determined with a HORIBA LA-960V2 utilizing the laser diffraction technique. Particle shape information was determined with the HORIBA LY-9610 Imaging Unit accessory, which sits in-line with the flow cell to additionally measure shape information through dynamic image analysis.

- Method
  - o Cell: Flow Cell
  - o Refractive index: 1.920-0.522i
  - o Circulation level: 3
  - o Agitation level: 3
  - o Dispersion Medium: Isopropyl alcohol (IPA)

Test Procedure:

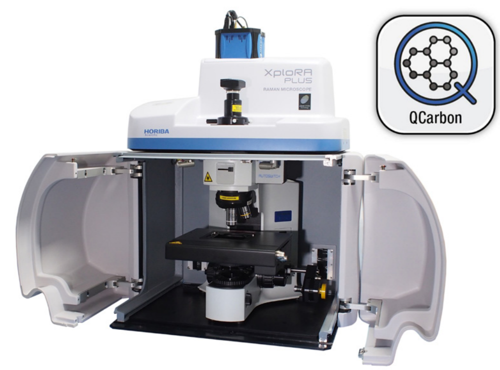
1. Feed the LA-960V2 with IPA.
2. Add sample to 90% transmittance.
3. (For LFP-2 sample) Sonicate for one minute on level 7.
4. Perform a measurement for size information.
5. Perform a measurement with the image accessory (LY-9610) for shape information.

Analytical Test Method for Raman Spectroscopy

Raman spectra were collected with a HORIBA XploRA™ PLUS Confocal Raman Microscope.

- Method
  - o Laser wavelength: 532nm
  - o Laser power: < 1 mW on sample
  - o Raman data sets: 400 points spectra for each sample

Raman spectra were processed by fitting peak models and extracting peak parameters from each spectrum by using a HORIBA Raman software LabSpec6 app called QCarbon.



The XploRA PLUS Confocal Raman Microscope.

Particle Size & Shape Distribution Results

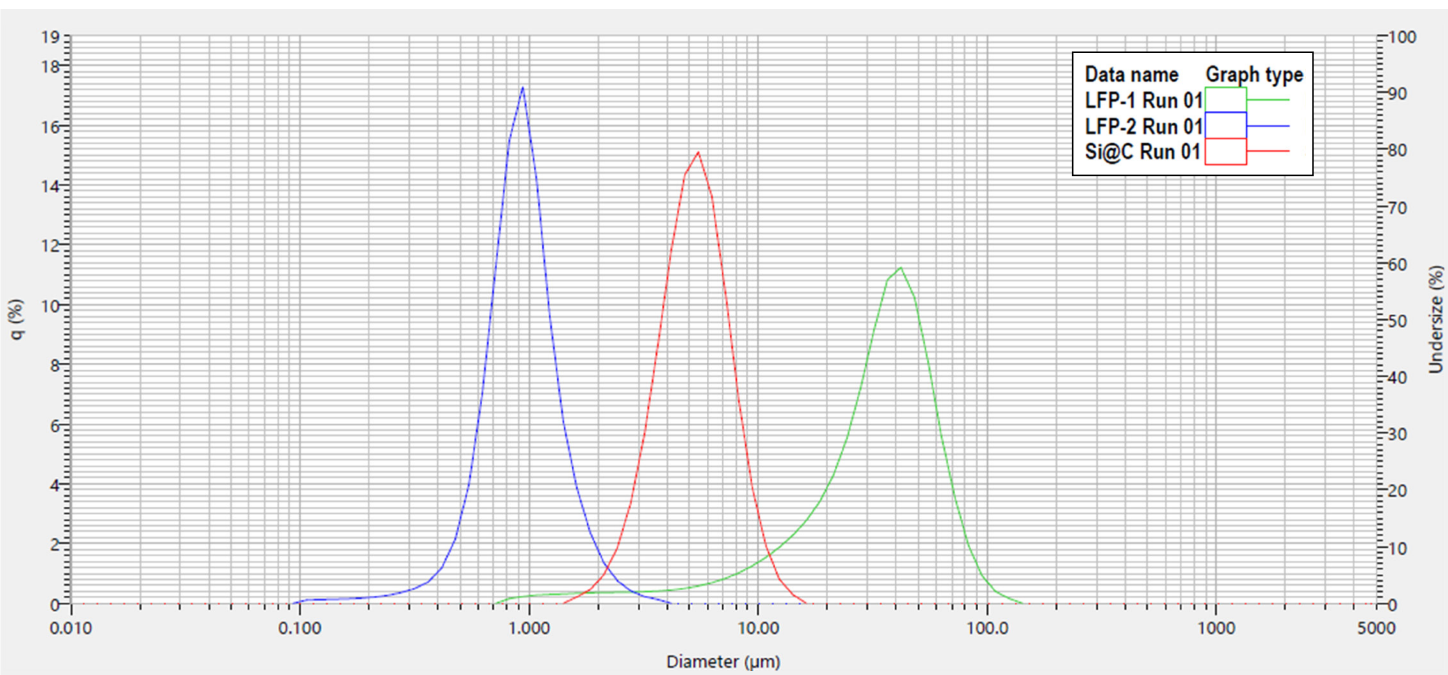


Figure 1 (above): Particle size distribution graph of carbon coated LFP and carbon-coated silicon materials by laser diffraction (LA-960V2).

Figure 2 (right): Particle size distribution data of carbon coated LFP and carbon-coated silicon materials by laser diffraction (LA-960V2).

Sample	D10 (µm)	D50 (µm)	D90 (µm)
LFP-1	10.95285	35.56009	62.72018
LFP-2	0.58444	0.92162	1.47895
Si@C	3.21320	5.25152	8.27677

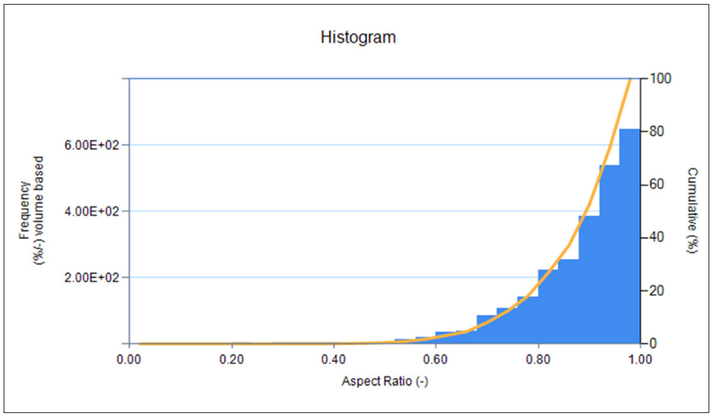


Figure 3. Aspect Ratio distribution graph (width/length) for LFP-1 from imaging unit accessory (LY-9610).

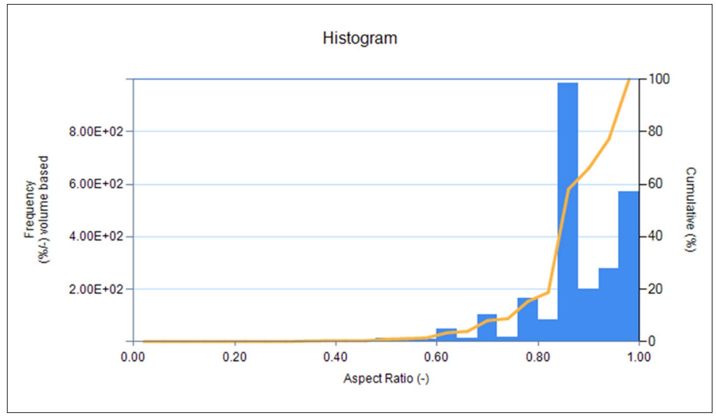


Figure 5. Aspect ratio distribution graph (width/length) for LFP-2 from imaging unit accessory (LY-9610).

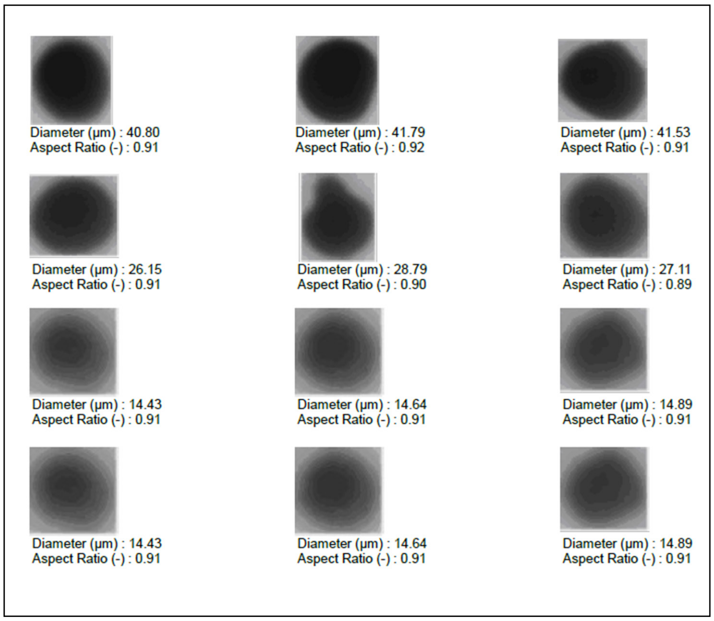


Figure 4. Particle image list for LFP-1 from imaging unit accessory (LY-9610).

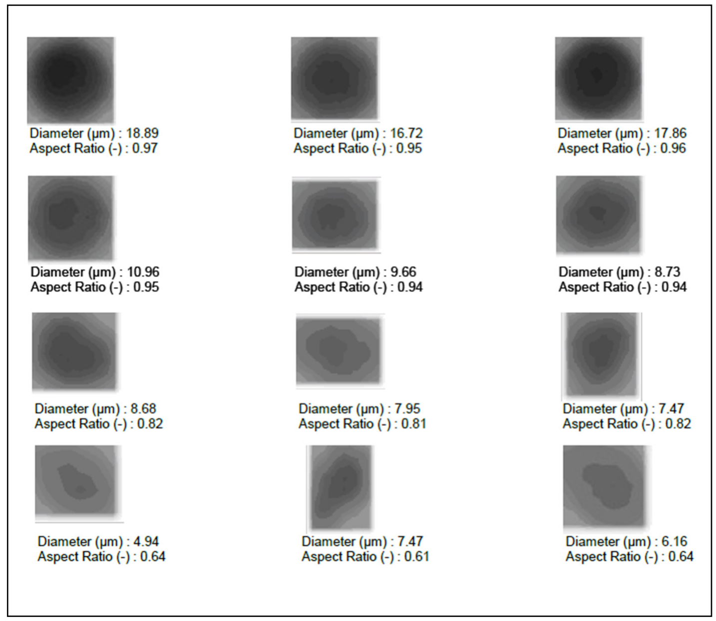


Figure 6. Particle image list for LFP-2 from imaging unit accessory (LY-9610).

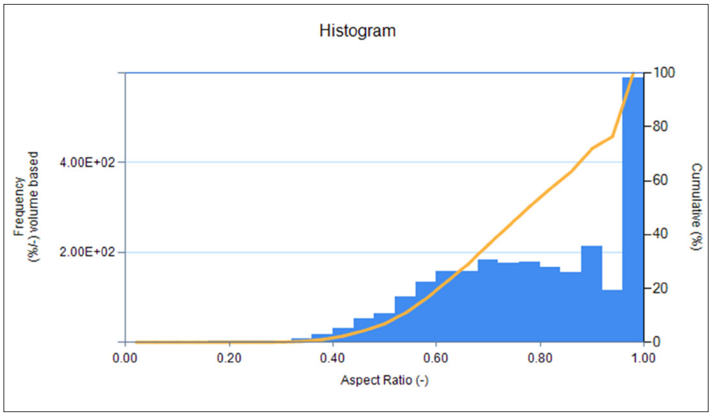


Figure 7. Aspect ratio distribution graph (width/length) for carbon-coated silicon from imaging unit accessory (LY-9610).

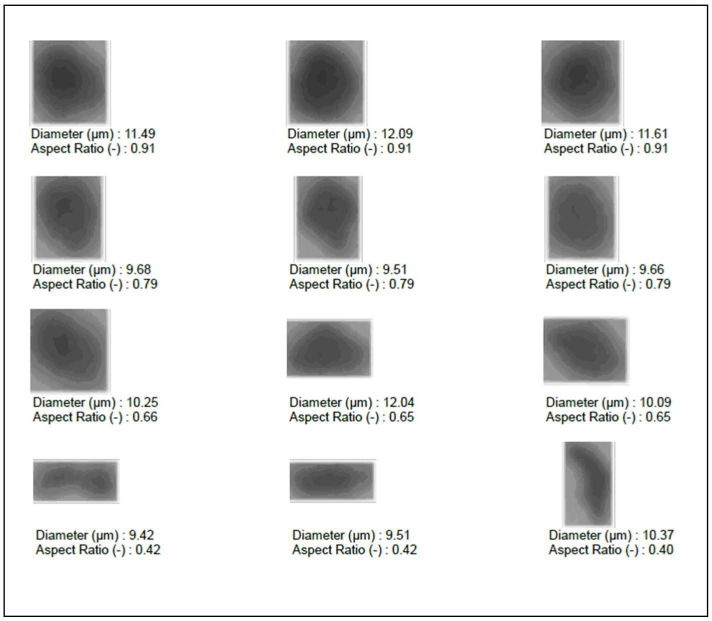


Figure 8. Particle image list for carbon-coated silicon from imaging unit accessory (LY-9610).

Sample	X10 (μm)	X50 (μm)	X90 (μm)
LFP-1	0.7392	0.9157	0.9902
LFP-2	0.7667	0.9431	0.9902
Si@C	0.5314	0.7510	0.9392

Figure 9. Aspect ratio distribution (width/length) from imaging unit accessory (LY-9610) for battery materials.

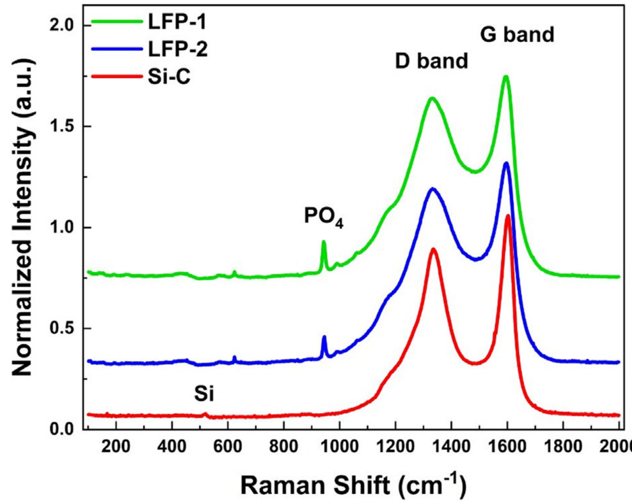


Figure 10. Raman spectra of carbon coated LFP and carbon-coated silicon materials.

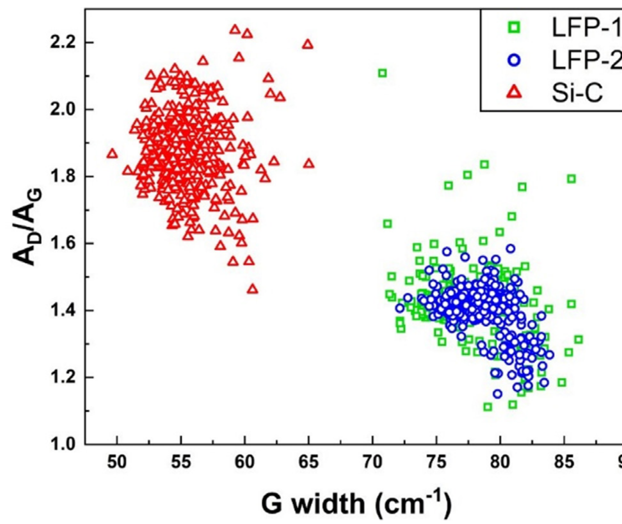


Figure 11. Scatter plot of A_D/A_G vs G width of carbon coated LFP and carbon-coated silicon materials (400 points of spectra for each sample).

Sample	A_D/A_G Mean	A_D/A_G StDev
LFP-1	1.427	0.094
LFP-2	1.408	0.066
Si@C	1.875	0.110

Figure 12. Raman spectroscopy A_D/A_G mean and standard deviation results for carbon coated LFP and Si materials.

Sample	G Width Mean	G Width St. Dev.
LFP-1	77	2.586
LFP-2	78	1.980
Si@C	55	2.143

Figure 13. Raman spectroscopy G Width mean and standard deviation results for carbon coated LFP and Si materials.

Discussion

LFP-2 shows a small and narrow particle size distribution, indicating a large available surface area for electrochemical reactions. LFP-1 has a tail of fine particles stretching down to 1 µm, which lines up with the fact that LFP-1 is the agglomerated, unprocessed form of LFP-2, which itself has a median of around 1 µm. Carbon-coated silicon shows a small, narrow size distribution as well, indicating good cell performance.

The shape information shows that both LFP-1 and LFP-2 have high aspect ratios, indicating high sphericity and higher packing density and higher volumetric energy density, while carbon-coated silicon has a lower aspect ratio, indicating the particles are less spherical and in general have a lower packing density and lower volumetric energy density. Visually, the particle image lists show more spherical particles for the LFP samples and more angular particles for the carbon-coated silicon sample.

For the Raman spectroscopy results, the LFP samples share similar A_D/A_G and G width results, indicating similar levels of defects and degrees of graphitization, showing that LFP-1 did not undergo significant chemical changes after being processed into LFP-2. LFP-1 shows a higher standard deviation for both the A_D/A_G and G width results, indicating that there are likely more agglomerates and variation in defects associated with LFP-1. The carbon-coated silicon sample shows vastly different A_D/A_G and G width results compared to the LFP results and indicate they underwent a different carbon coating process.

The G width mean is lower for carbon-coated silicon compared to the LFP samples, indicating that the graphite in the carbon coating for the silicon displays a higher degree of graphitization. All the samples exhibit a high D band, indicative of many defects/doping in the carbon structure of the coating.

In addition to the graphite D and G bands, a P–O bond of PO_4^{3-} can be seen in the LFP spectra around 946 cm^{-1}, and its height gives a sense of the thickness of the carbon coating, with the P-O band of LFP-2 having a lower height indicating a thicker coating. Similarly, a Si band can be seen in the carbon-coated silicon spectrum around 520 cm^{-1}, which can be used to compare carbon coating thicknesses of similar carbon-coated silicon samples.

Conclusion

The results show that the physical size and shape parameters of battery materials such as the diameter and aspect ratio are important indicators of available surface area and volumetric energy density. In addition, the chemical parameters of the carbon in the graphite coating can be tracked through the A_D/A_G ratio and G width, which monitor the level of defects and degree of graphitization respectively, impacting the electrical conductivity, capacity rates, and structural quality.

The HORIBA LA-960V2 laser diffraction particle size analyzer along with the in-line LY-9610 imaging unit accessory can be used to measure the size and shape characteristics of bulk powder battery material, while the HORIBA XploRA PLUS Confocal Raman microscope can be used to track the level of defects and degree of graphitization of the carbon coating of the battery materials.