

Surface Area Determination of Battery Cathode and Anode Materials

Relevant for: Battery anode & cathode materials, surface area

Corporations and professionals in the battery industry are always in search of the most efficient and safe battery technologies to fuel the energy needs of our world today and into the future. In order to optimize their design efforts, battery developers rely on accurate characterization of the physical properties of the components used in their designs



Figure 1: Batteries are used to power many consumer products. Optimizing the efficiency of the batteries requires accurate characterization of the materials used to manufacture them.

1 Why measure the surface area of battery materials?

Surface area is a critical property for battery components including anodes, cathodes, and even separator materials. Surface area differences affect performance characteristics such as capacity, impedance, and charging and discharging rates. Deviations from expected surface area can also indicate impurities or undesirable particle size for component manufacturers.

Using the NOVAtouch, the specific surface area (SSA) of the components and raw materials used in manufacturing batteries can be accurately and reproducibly measured. This information allows the developers and manufacturers of batteries to better control the performance, quality, and consistency of the end products.

2 Which instrument is used?

For this analysis of the SSA, also referred to as the BET surface area, the NOVAtouch gas sorption analyzer is recommended. This instrument has integrated sample preparation stations for degassing the sample to prepare the surface for

analysis, eliminating the need for external accessory degasser units. The independent operation of the degas stations and the analysis stations allows one set of samples to be analyzed while degassing the next set of samples. The four degas and four analysis stations allows for the high throughput critical in a quality assurance process.

3 Which samples are tested?

Materials used for anodes, cathodes, and separators vary in quality, purity, and textural properties, all of which affect the performance of the battery. For this report we chose two materials used for battery electrodes to illustrate how the surface area can be measured. The samples used are Lithium Nickel Cobalt Manganese oxide (LiNiCoMnO_2), used as a cathode material, and graphite, a typical anode material.

4 Measuring the samples

The most widely used means of determining SSA is the method developed by Brunauer, Emmett, and Teller in 1938 [1], referred to as the BET method. This method uses gas sorption data to determine the number of molecules of adsorbate in a monolayer on the surface of the material. If the effective cross-sectional area of adsorbate molecule is known, it is a simple calculation to determine the total surface area m^2 of the sample. This value is normalized to the mass of the sample m^2/g to make it independent of sample size.

4.1 Sample preparation

In order to accurately determine the surface area, it is important to start from a clean dry surface to avoid interference with the adsorbate. The NOVAtouch has four built in degas stations for sample preparation. Typically, samples are heated under vacuum for sufficient time to remove the pre-adsorbed water and

other gasses. An alternative method involves flowing dry nitrogen or helium over the sample while heating. The samples in this study were degassed at 200°C for 3 hours under vacuum.

4.2 Sample analysis

The BET method specifies acquiring data over the relative pressure range of 0.05 to 0.3 P/P_0 . Although a single point can be used to estimate the SSA, a more accurate value can be obtained using a multi-point BET method with at least 3 points. For this study 11 points were used. Other parameters are summarized in [Table 1](#) and their effect on the analysis discussed in [section 6](#).

Parameter	Used	Comments
Sample cell type	9mm large bulb with filler rod	9mm or 12mm stem to facilitate sample loading
Sample mass	~2.0–2.5g dry weight	Typically 0.5g to 5g, depending on surface area
Outgassing mode	Vacuum mode	Alternatively dry purge (flow) can be used
Operating mode	Helium mode	Alternatively NOVA mode can be used
Thermal delay	300 seconds	Depends on sample size
Equilibrium pressure tolerance	0.05 torr	Typical
Equilibration time	60 seconds	Typical
Equilibration timeout	120 seconds	Typically twice the Equilibration time
P_0 type	" P_0 calculate"	To reduce analysis time
Adsorptive	Nitrogen	Typical for BET method
Analysis Temperature	77.35 K	Boiling point of liquid nitrogen. This will vary with altitude and atmospheric pressure.

Table 1: Analysis parameters for battery materials.

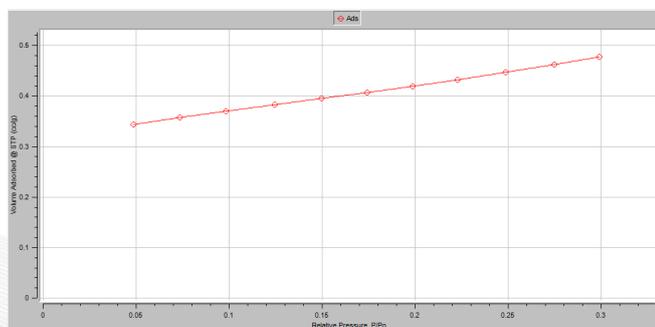


Figure 1: Eleven point isotherm of LiNiCoMnO₂, Sample 1.

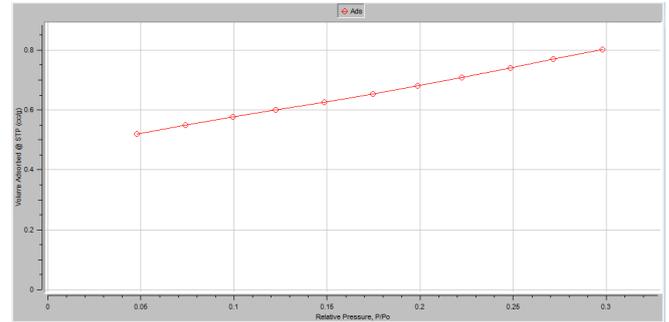


Figure 2: Eleven point isotherm of LiNiCoMnO₂, Sample 1.

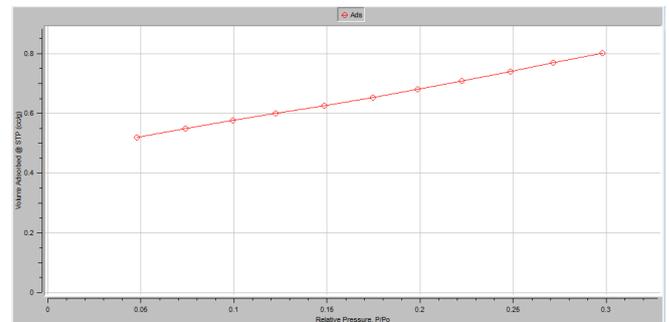


Figure 1: Eleven point isotherm of graphite, Sample 2.

Result Summary	
Isotherm Branch	Adsorption
Slope	2375.88
Intercept	2.1111
Correlation coeff, r	0.999987
C constant	1126.42
Surface area	1.46448 m ² /g

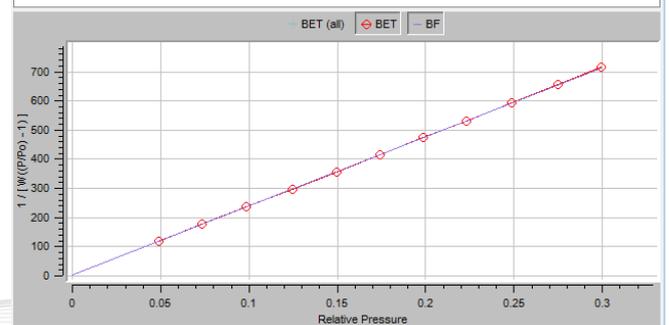


Figure 2: Eleven-point BET plot for LiNiCoMnO₂.

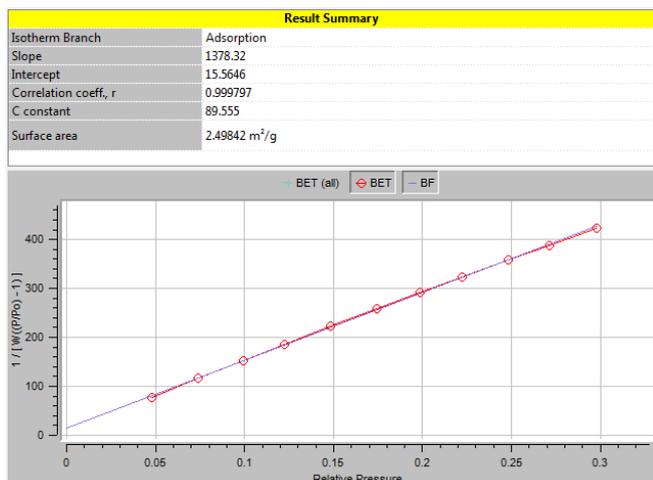


Figure 3: Eleven-point BET plot for graphite.

5 Results

For both samples the BET specific surface area (SSA) was calculated using the entire range of P/P_0 values measured. Close examination of the BET plots, especially for the graphite in **Figure 5** shows some non-linearity over the full range of 0.05 to 0.3 P/P_0 . Although the deviation from linearity is minor and the correlation coefficient (r) indicates a very good fit, using only the points in the linear range gives a more reliable and reproducible result.

The NOVAtouch software provides a method of determining the linear range of a BET plot in a reproducible and unambiguous way. This method is described elsewhere [2]. **Table 2** shows the results of the BET calculation done over the (i) full range, (ii) the range determined by the software, and (iii) a single point BET method for comparison. The correlation coefficient, (r), which indicates the degree of linearity in each range, is given in **Table 3**.

Sample	SSA (i) 11 points m ² g ⁻¹	SSA (ii) 6/7 points m ² g ⁻¹	SSA (iii) 1 point m ² g ⁻¹
1	1.464	1.476	1.458
2	2.498	2.786	2.451

Table 2: BET specific surface area of the two samples calculated using points in the three ranges described in the text.

Sample	r (i) 11 points	r (ii) 3 points	r (iii) 1 point
1	0.999987	0.999999	N/A
2	0.999797	0.999968	N/A

Table 3: BET correlation coefficient of the two samples calculated using points in the three ranges described in the text.

For both these samples the BET results for all three computed ranges show remarkable stability across the range of experimental values used in the calculation. This is to be expected from the very small deviation from linearity when using all 11 points.

In developing new materials, it is preferred to use the most linear region for the SSA determination, however, for quality assurance, where reproducibility and speed are most important, the single point BET produces a reliable result. If only one datum point is acquired, the analysis can be much faster. The NOVAtouch gives the flexibility to either method.

6 Effect of Experimental Parameters

Many experimental parameters and conditions can be adjusted to improve the quality of the data. These parameters and their effects are discussed here.

Sample cell type:

For ease of loading and emptying sample into and from the cell, a 9 mm or 12 mm stem cell should be used and the “large bulb” type allows for large amounts of sample if the surface area is small. The large bulb cell is also less likely to elutriate during evacuation. A smaller bulb cell can be used if the samples are in pellet or granular form and the surface area is high. A filler rod should be used for the analysis to reduce the void volume (but should NOT be used during degassing as it increases the risk of elutriation).

Sample mass:

Typically, 0.5g to 5g are taken according to the anticipated specific surface area. If possible, it is preferred that there be 2–5 m² of total surface area in the cell. Unnecessarily large sample masses lead to excessive analysis times.

Outgassing mode:

It is acceptable to prepare the sample under a flow of dry inert purge gas (such as nitrogen or helium) or by evacuation for the requisite time. It is important to keep the temperature below the point where the surface begins to change, due to decomposition, melting, or sintering.

Operating mode:

Using pre-calibrated cells (NOVA mode [3]) reduces

the time for the analysis. When using NOVA mode, the operator should know the true density of the sample and enter it when prompted or select “measure volume” as the method for correcting the empty cell calibration. Using helium eliminates the need for both cell calibration and knowing the sample density.

Thermal delay:

The time that the sample is pre-cooled before the actual measurement phase begins is adjust-table. Longer times ensure full thermal equilibrium and highest quality results but reduce sample throughput. Shorter times avoid the negative effect of too long a time in liquid nitrogen but can lead to non-linearity in the BET data.

Equilibrium pressure tolerance:

Sufficiently tight tolerance should be set for equilibrated data without causing undue delay. A value of 0.05 torr is reasonable in most cases.

Equilibration time:

Since equilibrium is detected by the instrument as when the pressure change over the “*equilibration time*” is less than the “*equilibrium pressure tolerance*”, Too long a programmed time will unnecessarily lengthen the total analysis time and, in the case of some samples, promote morphological change. 0.1 torr in 60 seconds is the same rate as 0.05 torr in 30 seconds, but the latter condition is actually met sooner, but more susceptible to signal noise.

Equilibration timeout:

If the sample is changing during the analysis, it may not achieve sufficient stability to meet the criteria of the equilibration pressure tolerance and can cause equilibration to take even longer than normal. This timeout curtails the process and causes the analysis to proceed at a more reasonable rate. The timeout value is typically twice the equilibration time value.

P₀ type:

P₀, the saturation pressure of the analysis gas at the analysis temperature, is required to calculate surface area as it relies on the relationship between the amount of gas adsorbed and P / P₀, the relative pressure of the gas. The BET method is very tolerant of small uncertainties in the P₀ value, so a very precise determination of it is not needed. Rather than having the NOVA touch measure P₀ while the sample is in liquid nitrogen, the “P₀ Calculate” or “P₀ Entered” modes are recommended

Adsorptive:

The gas used to probe the surface of the sample is traditionally nitrogen; however, in some cases argon can be used.

Analysis Temperature:

The analysis temperature is generally at the boiling point of the adsorptive to allow analysis to the saturation pressure. For nitrogen this is 77.35 K and for argon it is 87.30 K.

7 Conclusion

The NOVA touch is perfectly suited for measuring the surface area of battery materials. Since a higher surface area increases the rate of lithium insertion / removal into/from the crystal structure of the electrodes, the surface area is an important characteristic to measure when optimizing the battery design and synthesizing novel materials for batteries.

8 References (1)

1. Brunauer, S., Emmett, P. H., & Teller, E. (1938). Absorption of gases in multimolecular layers. *J Am Chem Soc* 60: 309–319.
2. Rouquerol, J., Llewellyn, P., & Rouquerol, F. (2007). Is the BET equation applicable to microporous adsorbents? *Studies in surface science and catalysis*, 49–56.
3. Lowell, S. (1994). *U.S. Patent No. 5,360,743*. Washington, DC: U.S. Patent and Trademark Office.

Anton Paar QuantaTec

Tel: +1 561 731-4999

application.qt@anton-paar.com

<https://www.anton-paar.com/quantachrome/>