Advanced Energy Storage Technologies

https://www.micromeritics.com/Product-Showcase/Battery-Tech.aspx

Lithium-Ion Battery Technology

The Lithium-ion battery is an energy storage device capable of almost continuous charging and discharging. In comparison to traditional battery technologies, lithium-ion batteries provide a significantly higher performance and efficiency In terms of application. The lithium-ion battery market can be segmented into consumer electronics, automotive, storage grid energy, and industrial use.

Improving global economic conditions, rising disposable income, the need for clean energy and surging demand for quality and uninterrupted power are a few of the major factors anticipated to boost demand for lithium-ion battery. The power density, safety, recharge time, cost, and other aspects of its technology are expected to continue to advance.



https://www.youtube.com/watch?v=JXHHUexcOvc

The Electric Car - Lithium Ion Battery Technology

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Electrode Analysis

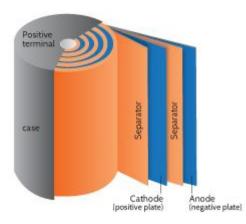


The development of cathode and anode materials for lithium-ion batteries is based on improvement to power and energy density as well as the thermal/chemical stability for enhancements in battery life and charge cycling.

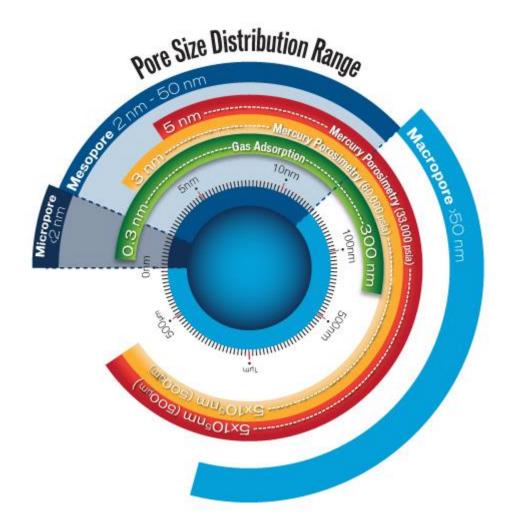
The theoretical capacity of a lithium-ion battery is determined by the materials used. In electrode processing, knowledge of particle morphology—including particle size, shape, powder density, porosity and surface area—have critical affect to manufacturability and the desired performance characteristics of the electrode.

Porosity Measurements

The electrodes porosity structure has a direct influence on particle to particle contact between the active material and the conductive diluent. Porosity is essential for the electrolyte to transport lithium-ions to and from the active materials of the electrode.



By controlling porosity, higher intra-electrode conductivity can be achieved to ensure adequate electron exchange as well as sufficient void space for electrolyte access/transport of lithium-ions for intercalation of the cathode. Porosity blocking/clogging during intercalation can lead to capacity fade.





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Particle Size/Particle Shape

Particle size influences capacity, cycling, and coulomb efficiency. Particle size will impact the amount of solid-state diffusion of lithium-ions that intercalate at the electrode. Smaller particles, especially nanoparticles, will lead to smaller volume changes upon cycling. This contributes to less mechanical stress, increased hardness, and greater resistance to fracture.

It has been reported that a broad particle size distribution may increase the energy density more than a mono-dispersed distribution.

Controlling and customizing particle size distribution can result in the ability to make available custom tuning that will result in high power (mono-disperse) or high energy density (poly-disperse).

Shape will affect packing density. Spherical shaped particles will pack more densely than fibrous or flake shaped particles. The average strain energy density stored in a particle increases with the increasing sphericality. Fibrous and flake shaped particles are expected to have lower tendency for mechanical degradation than the spherical shaped particles.







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Surface Area

Increasing the surface area of the electrode will result in improvement in the efficiency of the electrochemical reaction and facilitates

the ion exchange between electrode and electrolyte, especially within the anode as higher surface area permits short diffusion paths to the lithium-ions between the graphite particles. Lower surface area materials are better suited for improved cycling performance of the cell resulting in

longer battery life.

Greater surface area does present some limitations due to the degradation interaction of the electrolyte at the surface and resultant capacity loss along with thermal stability. Nanoparticles hold much promise to increase surface area without capacity loss. This facilitates fast charge and more efficient discharge rates and improves the capacity of the battery.

Separator / Binder Evaluation

Separator/Binder Evaluation

The separator permits ion flow from one electrode to the other while preventing any electron flow, essentially separating the anode from the cathode.

The typical separator is made up of polyolefins, usually polypropylene and/or polyethylene, along with other polymers, ceramics, and ceramic/polymer blends.

Separators are highly porous, typically

>40% porosity, approximately 25 µm thick and exhibit low ionic resistivity. Layered or composite

separators are used as safety devices to prevent thermal runaway of the cell.

Binder materials are used to hold the active electrode material particles together and in contact with the current collectors, i.e. the Aluminum Foil of the cathode or the Copper Foil of the anode.



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Density/T.A.P Density

The density of the graphite anode has an effect on its ability to withstand degradation under challenging load and discharge operations. A higher anode electrode particle density decreases the porosity resulting in a lower active surface area of the electrode. This reduces the electrode/electrolyte contact area.

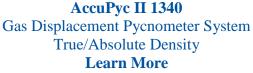
True/absolute density and envelope density can help by determining electrochemical performance attributed to the electrodes available porosity for intercalation.

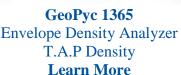
A clear correlation has been foundbetween irreversible capacity and internal pore volume.

T.A.P. density measurement is an important indicator of volumetric energy density. A low T.A.P. density translates into a low volumetric energy density where the converse indicates a high

volumetric density. Higher T.A.P density permits denser electrode films (more active material per unit volume) to be made for coating the electrode.







Pore Size, Shape, Distribution & Tortuosity

The size, shape, and tortuosity of the electrodes pores will significantly affect lithium ion transport rates through the electrolyte retained within this porous structure. Electrode microstructure resulting from the manufacturing process has direct influence on energy density, power, lifetime, and reliability of the lithium-ion cell.

A better understanding of the interconnectivity of adjacent pores, closed pores, and channels that may be created during the manufacturing process helps to ensure optimal electrolyte and electrode interaction. Knowing the tortuosity of a porous electrode and electrolyte interface makes it possible to determine if cell performance limitations are due to its microstructure.



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Porosity Measurements

Specification of percent porosity is an important parameter in the acceptance criteria for the separator. The separator must have sufficient pore density to hold the liquid electrolyte that supports ionic movement between the anode and cathode. Higher porosity means less heat generated in the cell and greater energy density.

Uniform porosity is essential to avoid variations in ion flow. The more variation in ionic flow within the separator, the greater the effect at the surface of the electrode and the quicker it will fail with a significantly decreased cycle life. Excessive porosity hinders the ability of the pores to close, which is vital to allow the separator to shut down an overheating battery.



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Pore Size, Shape , Distribution, and Tortuosity

The separator pore size must be smaller than the particle size of the electrode components, i.e. the electrode active materials and any conducting additives. Most separator membranes contain submicron pore sizes that block the penetration of particles.

Uniform distribution and a tortuous structure of the pores are also a requirement. Uniform distribution prevents uneven current distribution throughout the separator and tortuosity suppresses the growth of dendritic lithium.



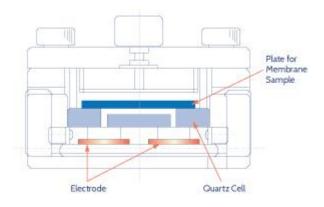
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Zeta Potential

To further understand the transport mechanisms of the separator membrane, zeta potential can indicate the membranes electrolyte affinity. This can permit fine tuning of battery performance to improve cycle life.

Cycle life is extended when the separator has a low electrolytic resistance but high aqueous permeability. Zeta potential can also provide needed information about the membranes affinity with electrolyte additives.





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ELSZ-2000 Solid Sample Cell Diagram





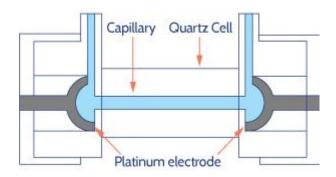
Liquid electrolyte plays a key role in commercial lithium-ion batteries to allow conduction of the lithium-ions between cathode and anode. The most commonly used electrolyte is comprised of lithium salt, such as LiPF6 in an organic solution.

High purity is required to prevent oxidation at the electrode and to promote good cycle life. In addition to lithium salt, various additives are also included in the final electrolyte solution. These additives are mixed with the LiPF6 solution to prevent lithium dendritic formation and degradation of the solution.

There are electro kinetic phenomena caused by charge separation at the separator-electrolyte interface. Diffusion of charged electrolyte solution through the pores of the separator has to undergo the influence of the zeta potential at the interface.

The zeta potential at that interface may impede or aid the passage of the electrolyte across the separator. The zeta value gives an indication of the potential stability of a system: the larger the value (positive or negative) the more stability of the solution.

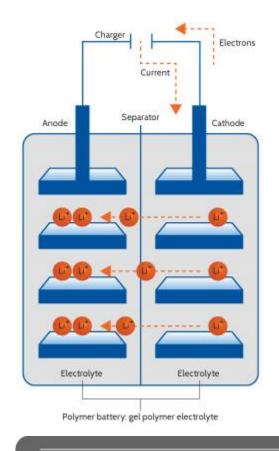




ELSZ-2000

NanoPlus HD Zeta Measurement Cell

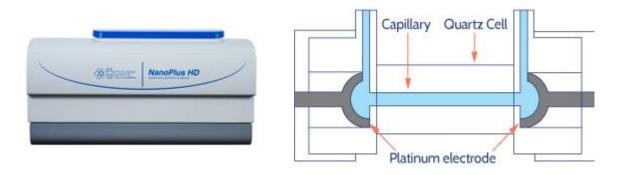
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Zeta Potential

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ELSZ-2000 HD Zeta Measurement Cell

Manufacturing and Failure Analysis



Materials characterization during and prior to manufacturing is a critical control parameter to ensure the optimal operation of cell components and the final assembled battery.

From raw materials to component manufacture and the assembled battery itself, material characterization plays a vital role in determining the desired electrochemical performance, safety, cell cycling and other important parameters.



Particle Size/Particle Shape-Raw Materials

Particle size and shape influences packing density which in turn affects electrode thickness and therefore energy density.

It has been shown that the particle size distribution of graphite, as well as particle orientation in the coated foil affects the

electrochemical performance of graphite anodes. Purity is also an important issue and low levels of metallic impurities must be maintained in all powders and additives used in electrode manufacture.



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Calendering/Solid Fraction Determination

Calendering is the most critical step in the production of high performance electrodes. Porosity and thickness of the electrode film will decrease with increasing calendering. Calendering would also be expected to change the pore structure of the electrode, which would thereby impact the wetting behavior of the film by the electrolyte.

Calendering beyond the optimum level

causes reductions in porosity and average pore diameter which can result in irreversible capacity loss, high rate cycling, and poor longevity in cycle performance.

Solid Fraction is a control parameter used

in roller compaction operations. This control parameter assists in determining the optimal setting for speed, compression and nip angle in the roller compactor.

Using the the solid fraction as a critical quality attribute will ensure consistent product batch to batch, along with the end product having the designed and desired electrochemical performance.

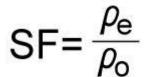




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Solid Fraction, Envelope and True Density SF= Solid Fraction (relative density)



 $SF = \frac{\rho_e}{\rho_o} \qquad \begin{array}{l} SF = Solid \ \text{Fraction (relative density)} \\ Pe = Envelope \ \text{Density of the Ribbon} \\ Po = Tru \ \text{Density of the Granule} \end{array}$

Performance Degradation

Over the life of a cell, physical and electrochemical occurrences contribute to degradation in performance. This drop in performance is most notably recognized through capacity fade during charge and discharge cycling or by reduced shelf life.

Expansion and contraction may cause interfacial stress that adversely effects the electrode performance, to the point that delamination may occur causing a reduction in contact between the electrode material and the current collector. Pore size changes can occur from this mechanical failure resulting in reduction in electrolyte contact and poor cycling behavior.



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