

# Applications for High Purity Alumina in Lithium-ion Batteries

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### Introduction

Lithium-ion batteries (LIB) are the ubiquitous global choice for rechargeable battery applications, including mobile phones, Electric Vehicles (EV) and Energy Storage Systems (ESS). They have been in production since the 1990's and improvements in safety and performance are continuously being made. Energy density has increased at around 3% per year and has now reached approximately 300Wh/kg and 750Wh/l. Despite this improvement more capacity and longevity is required to meet the ever-increasing power demands of the mobile communication devices and EV applications. In particular, it is increasingly important to maximise the cycle life and minimise the capacity fade of the cells – this will increase the cumulative capacity and lifetime of the cells. This in turn reduces the requirement for new raw materials to supply the increasing demand for batteries.

Despite their global usage, current LIB systems are not fully stable due to phenomena such as reactions of the solvents with the anode, cathode structural changes with cycling, loss of elements from the cathode compounds, decomposition of the electrolyte salts and others.

High Purity Alumina (HPA) can play a role in several crucial aspects of the LIB system to enhance safety, decrease anode and cathode degradation reactions and increase cell lifetime. HPA can be applied to the battery separator and as coatings on the graphite (and silicon graphite composites) anode and on the cathode. This report will highlight a brief description of the application of HPA to these three areas of the cell and the afforded benefit.

AEM addresses this application through the operation of a clean process run on 100% renewable energy, certified (pending) according to ISO9001, 14001 and 45001, with minimal processing additions – hydrochloric acid is the only process chemical, which is recycled from the latter steps of the process.

A purified secondary product – aluminium chloride hexahydrate (ACH) is also produced. The process ensures no foreign metallic inclusions or transition metal compounds are present in the product.

Increased wettability and rapid absorption of electrolyte  
Thermal stability of the separator and  
Increased temperature range before shrinking,  
Enhanced resistance to oxidation of the polymer substrate  
Reduced self-discharge rate and  
Preserved or enhanced McMullen number.

### HPA as a battery separator coating

A typical lithium-ion battery contains a separator. LIB separators are essential for the safe and effective functioning of the cell. They have specific properties and must be engineered to meet strict criteria of strength, pore size, thermal resistance, lithium-ion conductivity etc.

LIB systems are required to be stable and retain capacity over many cycles of oxidation/reduction and years of operation, for this reason they require the use of high purity materials to ensure adequate performance and safety. Safety issues do not always manifest during production testing and may only become apparent themselves after many cycles of operation. LIBs are susceptible to the formation of dendrites which can lead to several problems within the cell, such as a simple loss of capacity and cycle life for soft short circuits and severe local heating due to hard shorts, which in turn can lead to thermal runaway and fire.

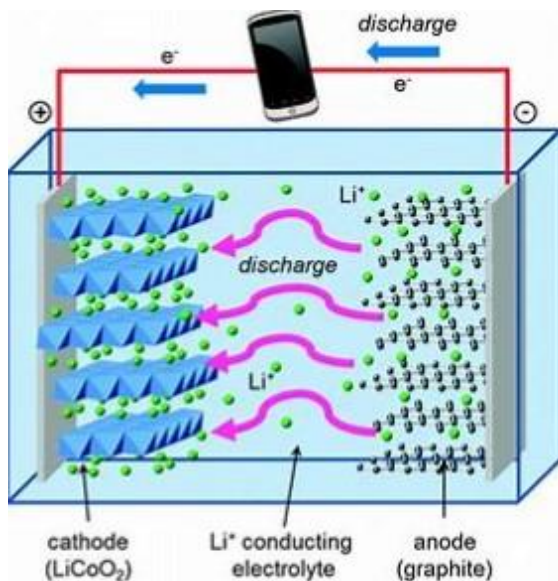
The two primary conditions for the formation of dendrites in lithium-ion batteries is provided as follows:

- a. Deposition of metallic lithium on the graphite surface on overcharge, deposition on the graphite of other, Transition Metals, from the electrolyte solution under normal charge/discharge conditions.

b. Transition metals leaching from conventional alumina can be a further source of dendrite initiation, which can be mitigated by high purity alumina, creating a strong value proposition for 4N and 5N products.

In addition to the issue of metal deposition and the formation of dendrites the impact of sodium impurity on the function of LiB is problematic. Traces of sodium can affect the cell capacity and cycle life by its influence on the Solid Electrolyte Interface - SEI- by causing it to thicken and increase in resistance. The AEM process yields very low sodium impurities due to the omission of the sodium hydroxide commonly used in the Bayer process for alumina production.

The application of alumina to the separator as a thin coating confers several performance and safety benefits to the cell.



#### HPA coating for Graphite and Silicon/graphite composite anodes

High purity (4N) graphite is the long-established anode of choice for LiB. Graphite is widely used because of its layered structure, high lithium insertion capacity (372 mAh/g,) high reversibility, and low cost. In addition, the low potential for Li insertion produces a high cell voltage, but the fast-charging capability is limited due to the potential for lithium plating on overcharge.

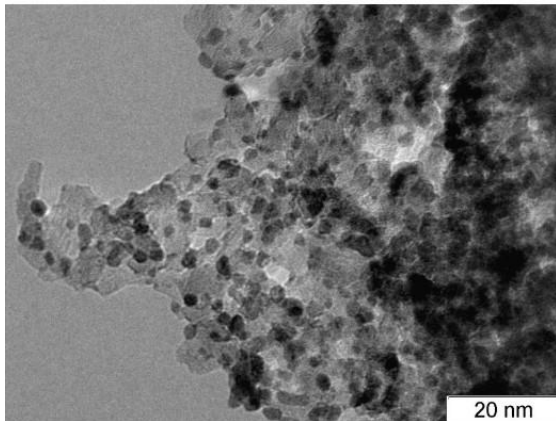
Anode capacity degradation is partially because of the reactions between the organic solvents of the electrolyte and the graphite. The solvent reacts

with the anode, forming solid or liquid layer at the graphite surface, the Solid Electrolyte Interface (SEI). This results in an irreversible capacity loss seen on the first cycle. This SEI layer is permeable and allows transport of ions from the electrolyte to the graphite surface. The thickness of the SEI will increase with time which increases the impedance of the interface and the overpotential of ions, so it will grow over time, which further deteriorates the battery and its life span. Failure of the graphite anode is due to the reduced reaction rate leading to power fade in batteries and capacity loss.

One of the methods to mitigate the degradation of the anode capacity loss is the coating on the anode particles with alumina. This has the effect of reducing the contact of the graphite surface with the electrolyte. This in turn cuts down the reaction of the electrolyte components with the graphite and prevents the loss of electrolyte, the build-up of a thick and increasing SEI. The alumina layer should be thin, in the order of a few nanometres, to ensure lithium-ion transport is not impeded. The alumina should be high purity so as not to add any problematic elements to the system. Improvements in cell performance such as a reduction in irreversible capacity loss and increased cycle life have been reported.

Battery manufacturers have very strict purity requirements for graphite to be used in LiB anodes. A typical purity level is 4N+. To ensure the overall purity level of the cell system is maintained, AEM is developing an easy high purity alumina coating method for graphite using a 4N+ pre-cursor which can be applied at scale and low cost.

Silicon and silicon/graphite composite anodes also require protection from degradation via electrolyte reactions and excessive expansion of the silicon, which leads to increased surface area, reaction with the electrolyte and isolation of the particles from the bulk material and current collector. In a similar way to the graphite only anode an alumina coating can protect the silicon from the electrolyte and increase the lifetime of the anode. The silicon and silicon/graphite composite can be treated in a similar process currently under development by AEM.



TEM image show layer of deposited material onto anodic material.

### HPA coating for LIB Cathodes

Lithium-ion battery cathodes are dominated by layered lithium metal oxides and predominately lithium nickel manganese cobalt oxides (NMC) with varying proportions of Ni Mn and Co. The industry is moving to high nickel materials and is reducing the cobalt content. The high nickel NMC compounds have good initial capacity, but nevertheless suffer from degradation during cycling. The loss of capacity is predominately a result of surface chemical changes which results in delithiation and loss of oxygen and a destabilised crystal structure. A volume change can also take place which induces cracks in the cathode particles which exposes more cathode surface to the electrolyte. In a similar manner to the graphite the cathode aids the decomposition of the electrolyte and may lead to surface films and the production of HF from the hexafluorophosphate salt. The resulting HF can dissolve cathode material further degrading the performance of the cell.

Surface coating of the cathode particles is a mitigation method to reduce the cathode surface interacting with the electrolyte. Coating the cathode powder also helps to prevent the structural changes in the NMC material and reduces the microcracking of the particles. All these mitigations contribute to increased capacity and cycle-life of the NMC. Several oxide materials have been investigated for cathode coating and alumina has been used successfully by several methods: vapour deposition, solution and dry mechanofusion application methods to reduce degradation

and improve performance. The coating thickness is dependent on the porosity of the coating. Continuous dense locating layers should be restricted to a few nm to be an effective barrier without degrading the cell performance. Porous, more particulate coating can be several tens of nm thick and give good results.

As a working hypothesis the mechanism of protection is primarily surface blocking by the alumina. Hence, a good, but not complete, coverage of the cathode particles is required to affect the long-term improvement in performance. Ideally, the coating should be an electronic insulator, and slow down cathode dissolution without impeding lithium ion transport to any significant extent. Electrochemical evaluation of optimized coatings shows a significant enhancement in rate performance and capacity retention by the optimal amount of coating material, while the solid electrolyte interface (SEI) and charge transfer impedance is decreased. Coating weight of around 1 wt% appears to provide the best results for alumina coated NMC electrodes.

In a similar manner to the graphite coating above the cathode coating material should at least match the purity of the cathode compound which is normally synthesised from 4N+ precursors.

Similar to the graphite situation, cathode purity is closely controlled and tightly specified to be produced from 4N precursor materials. AEM is currently developing a cathode coating process where the alumina is formed on the surface of the cathode particles from a 4N+ precursor.

### [AEM products for batteries](#)