White Paper

High Purity Alumina (HPA) Application on Lithium Ion Battery Separator

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11 May 2020

Executive Summary

As one of the major lithium ion battery components, battery separators play an essential role in safe battery operation. The vast majority of the traditional lithium ion battery separators are made from polyolefin membrane. The polyolefin membrane has a low melting temperature, typically less than 160°C. With the recent trend to increased battery energy density, the polyolefin membrane separator cannot meet the safety requirements. Historically, the failure of the lithium ion battery has led to recall of millions of laptops and mobile phones. Most of the battery failures were due to the thermal runaway caused by separator damage directly or indirectly.

Ceramic powders are now widely used to enhance the separator safety performance by coating on a traditional polyolefin membrane, or on electrode laminate, or as a material for fabrication of inorganic composite membranes. The ceramic layer will maintain the integrity of the separator during a temperature rise, and hence prevent thermal runaway.

Among the ceramics used in the separator enhancement, alumina (Al_2O_3) powder, especially high purity alumina (HPA), is one of the most widely accepted ceramic materials due to its unique properties. Alumina is electrically non-conductive and inert to all the chemicals present in the lithium battery components. Alumina is thermally conductive and thermally stable over a wide range of temperatures which are far beyond the battery operating temperature. These properties make it ideal for application as a coating and additive material for battery separator production.

The requirements of the alumina must be pure (typically 99.99% purity) enough, hence metallic cation impurities and metal impurities are less than a few ppm. Impurities may be leached to the electrolyte and later form dendrites during the battery operations, or form nuclei which accelerate dendrite formation. Metals in the ceramic layer, either introduced by the raw material and during the manufacturing process, or formed during operation, are the source of short-circuits. The impurities present in the ceramic layer are more harmful due to their close proximity to the polymer membrane.

A test by a German prestige research institute, Fraunhofer ITKS at Dresden, supports the claim that 4N HPA (99.99%) powder is the right material for battery applications. In a lithium ion battery, liquid organic electrolytes are used as a lithium ion transfer medium within the battery. Any impurities in the electrolyte can potentially reduce the battery cycle performance and lead to formation of dendrite, a major cause of short-circuit and thermal runaway. Impurities can be introduced from the alumina used for separator production.

The test by Fraunhofer ITKS has shown that impurities such as sodium ions in low quality alumina (99.8%) and boehmite can be leached out by, and contaminate the electrolytes. No electrolyte contamination was observed from the 4N high purity alumina.

Introduction to Lithium Ion Batteries

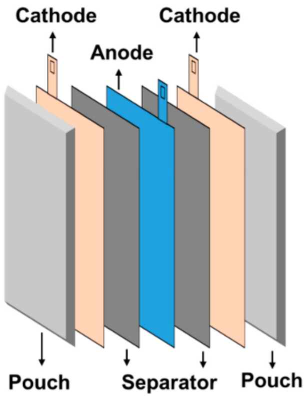
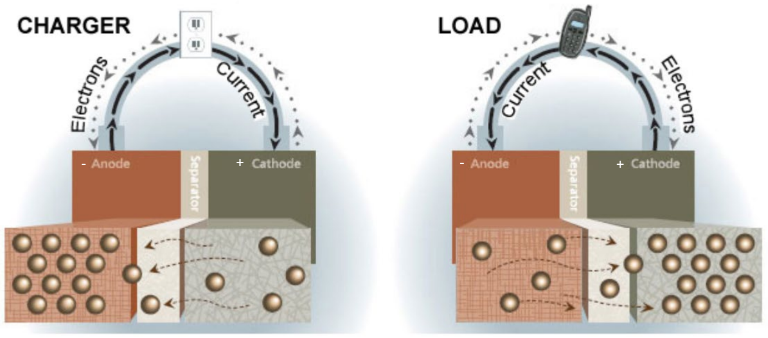


Figure 1: Li-Ion Battery

A typical lithium-ion battery consists of four major components: cathode, anode, separator and electrolyte (Figure 1). The cathode material is lithium containing crystals where lithium ions can desert and insert during battery charging and discharging. The anode is typically made from natural or artificial graphite. The separator is a porous membrane made from polymer (PE or PP), sometimes coated with a layer of ceramic particles. Electrolyte is a mixture of carbonate-based solvents with dissolved lithium salts.

In a battery cell, the cathode is coated on an aluminium foil while the anode is coated on a copper foil. The aluminium and copper foils are current collectors, where electrical current is conducted during battery charging and discharging. The separator, as a current insulator, is sandwiched between the cathode and anode layers to prevent short circuiting. After a battery is packed into its case, liquid electrolyte is added to fill up the voids in the battery. The electrolyte acts as a medium allowing the lithium ions to move from the cathode through the pores of the separator to the anode during charging, and vice versa during discharging (Figure 2).



Lithium-ion Rechargeable Battery
Charge Mechanism

Lithium-ion Rechargeable Battery
Discharge Mechanism

Figure 2: Charging and Discharging Mechanism for a Li-Ion Battery

Lithium Ion Battery Separator

The separator does not participate in any cell reactions, but its structure and properties affect the battery performance, including the energy and power densities, cycle life and safety.

A variety of separators have been used in batteries over the years. Starting with cedar shingles and sausage casing, separators have been manufactured from cellulosic papers, wood and cellophane to nonwoven fabrics, foams, ion exchange membranes, and microporous flat sheet membranes made from polymeric materials.

Nowadays, lithium-ion cells predominantly use microporous membranes made of polyolefins, that is, polyethylene (PE), polypropylene (PP), or laminates of PP and PE due to their mechanical properties, chemical stability and acceptable cost. Commercial microporous polyolefin membranes have a thickness of less than 30μm and pore size in the range 0.03-0.1 μm, and 30-50% porosity (Arora and Zhang, 2004). In the current technologies, around 25.4 μm (1mil) seems to be the standard thickness for consumer rechargeable batteries, and 40% is the typical porosity (Zhang, 2007). The separators have low ionic resistivity (1.5-2.5 Ω-cm2) and have bulk puncture strengths >300 g/mil.

Under conditions of excessive heat, a shut-down occurs by closing the pores of the Li-ion separator through a melting process. The polyethylene (PE) separator melts when the core reaches 130°C (266°F). This stops the transport of ions, effectively shutting the cell down. Without this provision, heat in the failing cell could rise to the thermal runaway threshold and vent with flame. This internal safety fuse also helps pass the stringent “UN Transportation Testing for Lithium Batteries” that includes altitude simulation, as well as thermal, vibration, shock, external short circuit, impact, overcharge and forced discharge tests.

As batteries have become more sophisticated, separator function has also become more demanding and complex. The shut-down mechanism does not always work as intended due to (a) dendrite growth that punctures the separator or (b) the separator shrinks in totality due to increasing charging temperature in the cell, resulting from ever higher energy density (Figure 3).

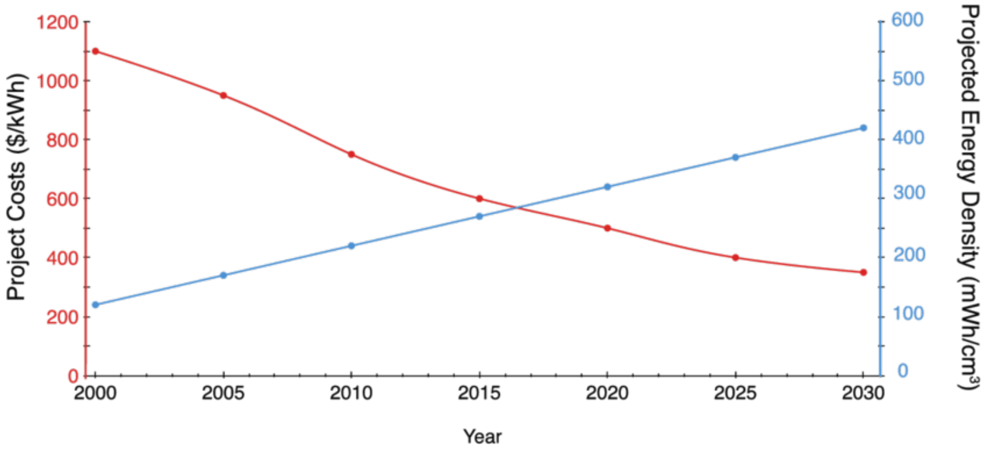


Figure 3: Li-Ion Battery Energy Density (The energy unit is power W (Watt) sustained over a given time h (hour). Density is the amount of energy that can be made available at a given weight kg (kilogram) or volume L (Litre) / cm^3 (cubic centimetre) of the battery, i.e. Wh/kg; or Wh/L; or Wh/cm^3) .

With increases in battery energy density, voltage and packing size, battery materials become less and less electrochemically stable. It is reported that an unusually thin monolayer and an aggressive increase in battery energy, plus other manufacturing defects in the battery used in the Galaxy Note 7 resulted in a total product recall of their Galaxy Note 7 mobile phone (Loveridge et al.,2018).

Figure 4. A Note 7 handset next to its charred battery after it caught fire during a test at the Applied Energy Hub battery laboratory in Singapore in October, 2017. (Edgar Su/Reuters)

HPA Enhanced Separators

To tackle the emerging safety issues of a commercial lithium ion battery, more complicated battery separators have been developed, including:

- ceramic coating on a traditional polyolefin membrane;
- inorganic composite membranes;

Among the ceramics used in the separator enhancement, alumina (Al_2O_3), especially high purity alumina, is one of the widely accepted ceramic materials due to its unique properties. Alumina is electrically non-conductive and inert to all the chemicals present in the lithium battery components. Alumina is thermally conductive and thermally stable over a wide range of temperatures which are far beyond the battery operating temperature range. These properties make it ideal for application as a coating and additive material for battery separator production.

Alumina coating on a PE/PP base sheets was invented by Celgard in 2000 (Zhang, 2002). Slurry of ceramic powder with binder and solution is coated on either one side or both sides of a base film of PE, PP or multi-layered PE/PP membrane (Zhang, 2002; Zhang et al., 2014). After drying, coated materials form a porous layer, including ceramic, which provides enhanced short prevention and excellent structural integrity at high temperatures. The thickness of the coated ceramic layers of a commercial Celgard separator ranges from 2 to 5 μm thickness.

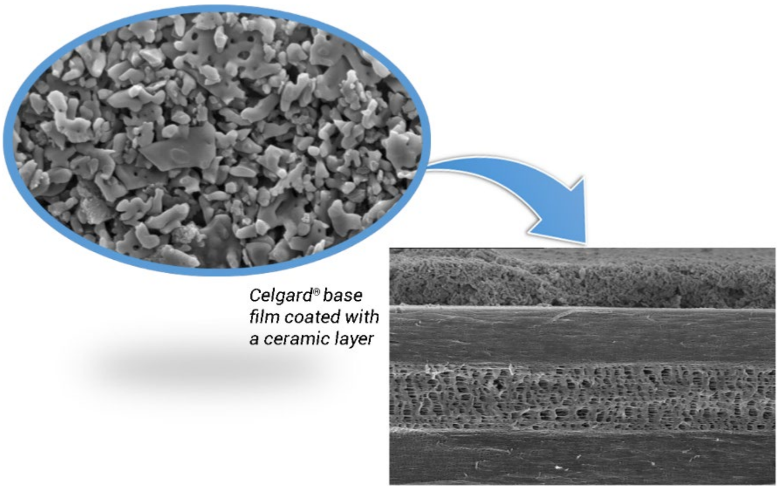


Figure 5. An Illustration of a Celgard Membrane Coated with 2 to 5 μm Thickness Ceramic Layers. (https://www.celgard.com/battery-innovation/ accessed 15 Dec 2015)

The presence of the alumina can significantly improve the physical and chemical properties of battery separators. The alumina coating layer may reduce or prevent dendrite puncture, lithium plating and separator shrinkage during over-heating, hence significantly increasing safety performance for a lithium ion battery.

Using a similar concept, a multilayered separator consists of an Al_2O_3 nano-powder layer and an electro-spun PVdF nanofiber layer coated on both sides of the polyethylene separator (An et al 2014). The Al_2O_3 layer provides excellent thermal stability as indicated by thermal shrinkage of only 7.8 % in area at 180 °C, and absence of a meltdown up to 200 °C.

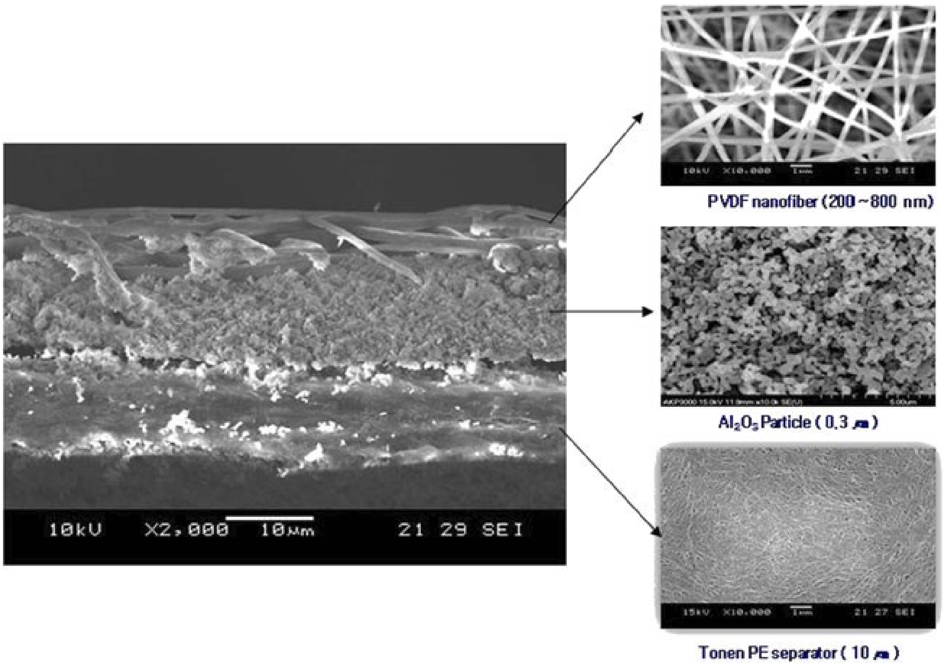


Figure 6. SEM Image of a Multilayered Ceramic Separator Consisted of an Al_2O_3 nano-powder layer (0.3 µm Sumitomo) and an electro-spun PVdF nanofiber layer coated on both sides of a 10 µm Thick Tonen polyethylene separator (An et al., 2014).

Alternatively, instead of coating alumina on a polymer separator basis, Samsung SDI patented a technology by coating the alumina layers on electrodes. The lithium ion battery using this technology exhibits a high thermal stability and shrinkage reduction at higher temperatures.

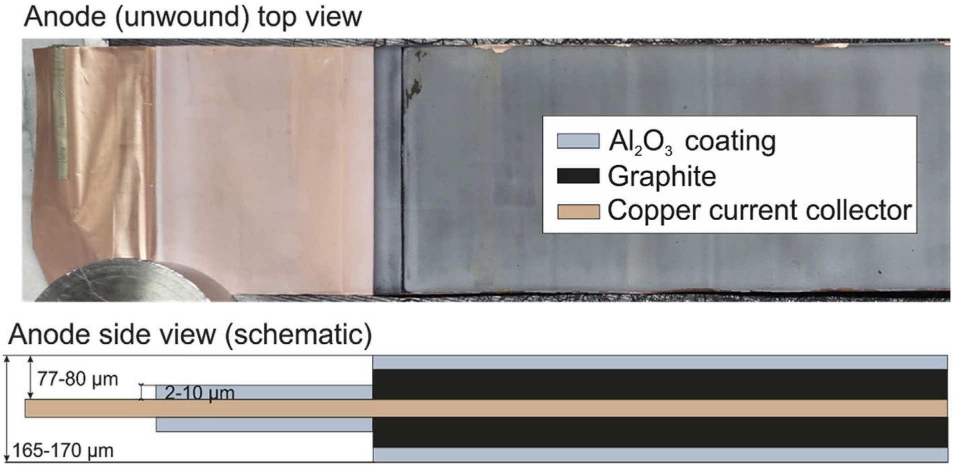


Figure 7: Anode of the Samsung SDI ICR18650-30A cell from cell opening from above and a schematic illustration from the side show the Al_2O_3 coating on anode surface and partly on the copper current collector. (Friesen et al. 2017)

Litarion Evonik (formally Degussa), a subsidiary of Electrovaya Inc, has introduced a new, thinner flexible ceramic separator, SEPARION®, for utility-scale and EV applications in 2015. SEPARION® separators are made from ceramics and a porous polyethylene terephthalate (PET) non-woven form a homogenous single-layer network. The ceramic coating is applied as a suspension onto a polymeric non-woven support; hence the ceramic material is embedded into the PET nonwoven support. The commercial SEPARION® separators have a thickness of 21 micron (P20) and 28 micron (P30). (Liu et al, 2003; Pascaly, 2010; Ayre, 2015; Morris, 2015)

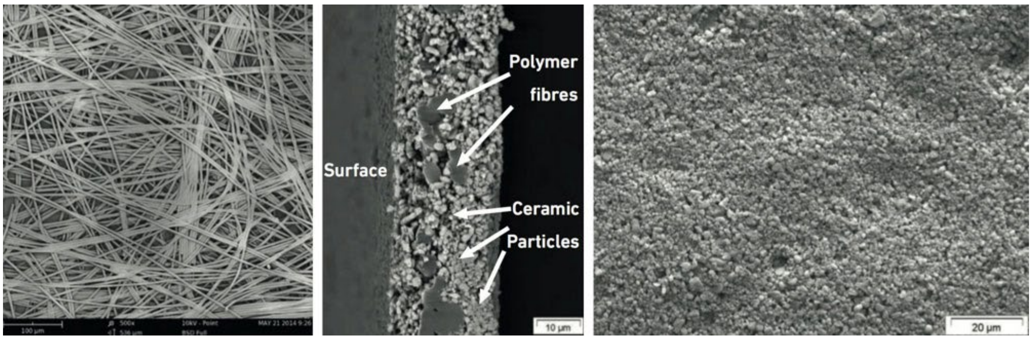


Figure 8: SEM images of PET non-woven, cross section of the SEPARION® S240P30 Alumina (Al_2O_3) separator, and surface. (Litarion, 2016)

Similar to that of the SEPARION® separator, the following companies are developing or producing composite separators using ceramic particles as filler:

- Freudenberg Performance Materials,
- ENTEK Membranes LLC,

- Asahi Kasei
- Porous Power Technologies (PPT)

Why High Purity Alumina?

Impurities such as metal and non-metallic foreign particles in direct contact with the separator causes a defect. The metal particles may damage the separator membrane causing a short circuit, or induce local defects which can create hot spots of locally high electrochemical activity that can lead to local lithium deposition and dendrite growth in a lithium-ion cell (Cannarella and Arnold, 2015). The dendrites in turn penetrate through the separator to cause a short circuit.

If a minor internal short occurs within a cell caused by a small contaminant penetrating the separator, local separator shutdown will effectively disable a small point within the cell by melting slightly and closing the separator pores (Figure 9) (Mikolajczak et al., 2011). Under some circumstances, this short-circuit leads to thermal run-way. Manufacturing methods become more critical as the battery cell energy density increases. With a separator thickness of only 20-25µm, any small intrusion of metallic dust particles can have devastating consequences (Battery University 2019&2020).

Figure 9: A Micro-shorting Location on a Separator, the size is approximately 1mm. (Mikolajczak et al., 2011)

To improve the separator performance and reduce the chances of thermal run-away, ceramic particles, mainly alumina (Al_2O_3) particles, are used to coat a ceramic layer on the PE/PP membranes. The coated alumina layers prevent failure at an elevated temperature and hinder the dendrite damage to the separator. The requirements of the alumina must be pure (typically 99.99% purity) enough, hence metallic cation impurities and metal impurities are less than a few ppm. Impurities may be leached to the electrolyte and later form dendrites during the battery operations, or form nuclei accelerating dendrite formation. Metals in the ceramic layer, either introduced by the raw material and during the manufacturing process, or formed during operation, are the source of short-circuits. The impurities present in the ceramic layer is more harmful due to its close proximity to the polymer membrane.

Fraunhofer ITKS Tests

Fraunhofer Institute for Ceramic Technologies and Systems (ITKS) in Dresden conducted a comparative test of electrolyte contamination by alumina with various purity grades.

Electrolyte used for the tests are Sigma Aldrich's battery grade 2.0 M $LiPF_6$ in EC/DMC= 50/50(% v/v) containing 0.5ppm sodium, Water < 15 ppm and Hydrogen Fluoride (HF) < 50 ppm. Three types of alumina and one boehmite sample were used for the tests. Of the alumina used, two samples are 99.8% grade with different sodium contents, and one 99.99% alumina sample as shown in Table 1.

Table 1: Major Properties of Alumina and Boehmite Used for the Tests.

Material	**Grade (%)**	**Particle Size D_{50} (µm)**	**Surface Area (m^2/g)**	**Sodium Content (ppm)**
Alumina 1	99.8	0.3-0.6	7.5	125
Alumina 2	99.8	1.5-1.9	1.5-2.5	74.7
Alumina 3	99.99	0.7	4.5	3.4
Boehmite	99	0.35	18	83

All solids were dried overnight at 105°C to remove any free moisture. Each types of solids were then mixed with electrolyte in a plastic bottle in a glove box to prevent any moisture ingress. The bottles with mixtures were then placed in a shaker for container shaking during the tests.

The initial electrolyte and solids mass ratio is 2.67. A 20 ml electrolyte sample was taken from each sample at a number of time intervals, and sent to an analytical lab for assaying. The last sample taken was at 792 hours (33 days).

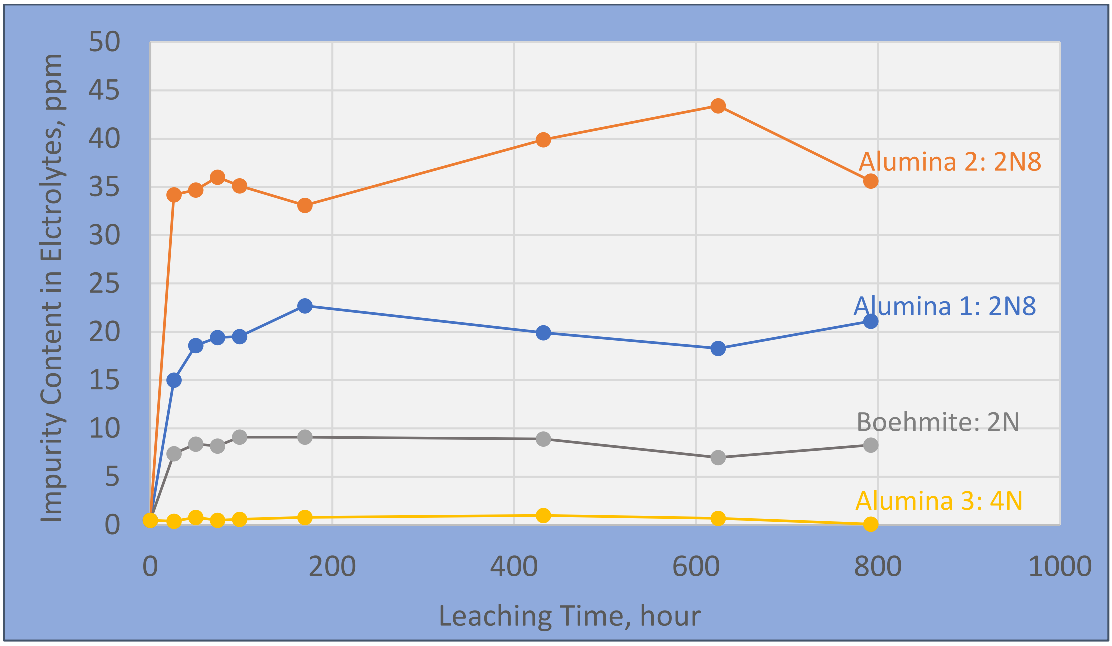


Figure 10: Sodium Impurities Leached to Electrolyte from Various Alumina and Boehmite

(Data MZS1 to be confirmed)

Testing found that sodium impurities in the solids samples is leachable under the tested conditions. The leaching of other elements into the electrolyte is insignificant. The worst results were measured in the Alumina 2 samples with sodium in electrolytes increasing to 35ppm from 0.5ppm. The sodium impurities in electrolytes with 4N material (Alumina 3) remained almost the same, as the alumina sample purity and initial sodium content mean there is almost nothing to leach out. The sodium leaching is a slow process and reached a maximum in around a week (170 hrs).

The colour change on the electrolyte samples was apparent from day 1. The original electrolyte samples are colourless. The dark colour in samples, as shown in Figure 11, is due to the contamination from leaching of alumina impurities.

Figure 11. The Electrolyte Samples Taken on Day 3. The Dark Colour Indicates the Samples with High Impurities

The test results clearly indicate that low quality alumina powders used in separator coating can bring in impurities, contaminating the electrolytes while the 4N high purity alumina has little contamination.

It is important to stress that water and HF impurities in the electrolyte can accelerate the leaching from alumina. To eliminate this influence, extreme care was taken to prevent any external water contamination. The alumina and boehmite powders were all pre-dried and handled in a moisture-free glove box. Only a small amount of HF and water exist in the original electrolyte samples. Nevertheless, sodium can still be leached out by the electrolytes, indicating the leaching of sodium is driven by the mass transfer rather than a chemical process.

It is well known that the sodium ion (Na^+) in lithium ion batteries impede the movement of lithium ions, and hence reduce the discharge capacity and battery life (Yamamoto et al., 2011; Paulsen et al.,2019). Under some circumstances, the sodium may deposit on the anode as metal or act as a catalyst to facilitate other metal deposition to form dendrite, a safety hazard.

Impurities in electrolytes have a negative impact on formation of solid-electrolyte interface (SEI), hence reduce the battery cyclability. Ube Industries, Ltd. discovered that if a small amount of impurities exists in the electrolyte, decomposition current generated from the impurities begins to flow, which leads to the formation of an undesirably thick SEI (Jow et al. 2014).

The majority of the leaching process happened in the first 24 hours of testing, indicating the electrolyte contamination can start immediately after electrolyte injection during the battery manufacturing process. The impurities may have impact on the formation of initial solid electrolyte interphase (SEI) at the “battery formation”, one of the last steps in the process of making battery cells. Battery formation is the process of performing the initial charge/discharge operation on the battery cell. During this stage, a special electrochemical SEI will be formed at the electrodes, mainly on an anode.

The low-quality alumina used in separator production has a negative impact on lithium-ion battery performance, while the 4N high purity alumina is the best material for the manufacturing of separator.

References

An, Min-Young, Hee-Tak Kim and Duck-Rye Chang (2014) Multilayered separator based on porous polyethylene layer, Al_2O_3 layer, and electro-spun PVdF nanofiber layer for lithium batteries, *J Solid State Electrochem*, Published Online: 20 Feb 2014.

Ayre, James (2015) Electrobaya-Litarion Introduces Separion p20 – New,Thinner Flexible Cenramic Separator for Lithium-ion Batteries, EV Obsession Web Site: https://evobsession.com/electrovaya-litarion-introduces-separion-p20-new-thinner-flexible-ceramic-separator-for-lithium-ion-batteries/ (accessed 03 Dec 2018).

Battery University (2019) Safety Concerns with Li-ion Batteries - Battery University, Updated 24 March 2019, https://batteryuniversity.com/learn/article/safety_concerns_with_li_ion (accessed 24/03/2020)

Battery University (2020) Lithium-ion Safety Concerns https://batteryuniversity.com/learn/archive/lithium_ion_safety_concerns (accessed 2 June 2020)

Cannarella, J. and Arnold, C.B. (2015) The effects of defects on localized plating in lithium-ion batteries. *J. Electrochem. Soc.* **162**:A1365–A1373.

Friesen, Alex, Stephan Hildebrand, Fabian Horsthemke, Markus Börner, Richard Klöpsch, Philip Niehoff, Falko M. Schappacher, Martin Winter (2017) Al2O3 coating on anode surface in lithium ion batteries: Impact on low temperature cycling and safety behaviour, Journal of Power Sources, 363(2017):70-77.

Jow, T. Richard, Kang Xu, Oleg Borodin, Makoto Ue (edit) (2014) Electrolytes for Lithium and Lithium-Ion Batteries, Springer, 6 May 2014, pp476.

Litarion (2016) SEPARION® Ceramic separators for large-format lithium-ion batteries, Latarion Brochure, Published Fed 2016.

Liu, J., A. Kahaian, I. Belharouak, S. Kang, S. Oliver, G. Henriksen, and K. Amine (2003) Screening Report on Cell Materials for High-Power Li-Ion HEV Batteries, Argonne National Laboratory Report No. ANL-03/16. Electrochemical Technology Program, Chemical Engineering Division, April 2003.

Loveridge, Melanie J., Guillaume Remy, Nadia Kourra, Ronny Genieser, Anup Barai, Mike J. Lain, Yue Guo, Mark Amor-Segan, Mark A. Williams, Tazdin Amietszajew, Mark Ellis, Rohit Bhagat and David Greenwood (2018) Looking Deeper into the Galaxy (Note 7), *Batteries* 2018, 4, 3.

Mikolajczak, Celina, Michael Kahn, Kevin White, Richard Thomas Long (2011) Lithium-Ion Batteries Hazard and Use Assessment, Final Report by Exponent Failure Analysis Associates, Inc., Fire Protection Research Foundation. July 2011.

Morris, Charles (2015) Separion P20 – a new flexible ceramic separator, Posted December 18, 2015 by Charles Morris & filed under Newswire, The Tech. on Charged Electrical Vehicles Magazine Web Site: https://chargedevs.com/newswire/separion-p20-a-new-flexible-ceramic-separator/ (accessed 03 Dec 2018).

Pascaly, Matthias (2010) Temperature Resistant Lithium Ion Battery Separators, Evonik Industries Presentation, February 22, 2010.

Paulsen, Jens, Heonpyo Hong, JinDoo Oh (2019) 14 [Na] Impurity Containing Cathode Material with Preferred Morphology and Method to Prepare from Impurities Containing Metal Carbonate. *US Patent* No.: US 2019/0386303 A1, Dec. 19, 2019.

Yamamoto, Manabu, Daisuke Nishikawa, Kazutoshi Ishizaki, Osamu Sasaki and Hideaki Sadamura (2011) Positive electrode active material particle powder, method for producing the same, and nonaqueous electrolyte secondary battery, *WIPO (PCT)* WO2011105361A1, September 1, 2011.

Zhang, S. S., 2007, A Review on the Separators of Liquid Electrolyte Li-ion batteries Journal of Power Sources, 164(2007):351-364.

Zhang Z. (2002) Separator for a high energy rechargeable lithium battery, United States Patent, No.: US6432586 B1, Date of Patent:: Aug 13 2002.

Zhang, Z. X. Li, L. Shi, P. Ramadass, P. M. Halmo and X. Zhang (2014) Separator membranes for lithium ion batteries and related methods, United States Patent, Pub No.: US2014/0045033 A1, Pub Date: Feb. 13, 2014.