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WHAT IS BATTERY GRADE LITHIUM CARBONATE?

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ABSTRACT

Currently there is no universal standard for the reporting of battery grade lithium carbonate analysis. It is common to hear that a lithium carbonate has been produced with a purity of > 99.5% but no clear understanding how this was determined or really what this means.

It is proposed in this paper to consider that a lithium carbonate sample could be described as having a lithium content or alternatively has a lithium carbonate purity. In the case of lithium carbonate content, the proposed formula is:

Lithium Carbonate Content = 100% – Water Content – Loss on Ignition – Acid Insolubles – Impurities.

In the case of lithium carbonate purity, it is proposed that the formula is:

Lithium Carbonate Purity = 100% – Acid Insolubles – Impurities

This helps to explain why a bicarbonated lithium carbonate, can have a lower lithium content while having higher purity. This is due to some bicarbonated lithium carbonates having a higher percentage of lithium bicarbonate.

It is also proposed that a standard suit of impurities be included the reporting lithium carbonate purity and that the detection limits, stated in this paper, using ICP and or AA, be used as a standard.

Regardless of the Lithium Carbonate Content and or the Purity, the purchasers of battery grade lithium carbonate will use their own maximum acceptable concentrations for key impurities. There is only one published standard by the Chinese (YS/T582-2006).

There is considerable difference in opinion amongst battery component fabricators as to what impurities in the lithium carbonate are harmful. The paper presents some commonly stated key impurities and their reported influence on battery performance.

Keywords: Lithium Carbonate, Battery Grade, Lithium Carbonate Purity, lithium battery performance, detection limits, Battery Impurities.

LITHIUM CARBONATE CONTENT

Lithium carbonate content is the main way converters specify lithium carbonate being offered for sale. The industry standard way is determined by the formula:

$$\text{Lithium Carbonate Content} = 100\% - \text{Water Content} - \text{Loss on Ignition} - \text{Acid Insolubles} - \text{Sum of the Impurities}$$

Formula 1

Essentially all the non-lithium carbonate species are deducted from 100%. As shown in the Formula 1 there are four deductions and in the section below each of the deductions is explained.

Water Content is the weight loss of the lithium carbonate sample when it is heated up to between 100 - 110°C. Effectively it is drying the sample and the water content can vary considerably depending on the way the sample has been stored or dried after being precipitated or crystallised. Typical values are 0.06 – 0.2 wt%.

LOI (Loss on Ignition) is the weight loss of the sample when the sample is further heated from 110°C to 500°C and held at 500°C until constant weight is achieved. The typical hold time assumed by laboratories to achieve constant weight is between 30 minutes to an hour. This should be confirmed on individual samples as it can also be influenced by particle size.

The weight loss in this temperature range is primarily due to the presence of lithium bicarbonate, or other bicarbonates, that may be present following refining of primary lithium carbonate. The thermal decomposition of lithium bicarbonate to lithium carbonate is represented by the following equation:



It should be appreciated that with increasing amounts of lithium bicarbonate in the product, the content (%) of lithium carbonate decreases. This is despite the material actually now containing significantly reduced concentrations of impurities. The logic for someone buying the lithium carbonate is that there is less lithium in the bicarbonate and they would prefer to maximise the amount of lithium in the material purchased.

The amount of bicarbonate varies widely and can be from almost 0 through to 0.4 wt%. In general, lithium carbonate that has been bicarbonated, to improve the quality, contains more bicarbonate, and hence will have a larger LOI.

The use of a TGA-DSC to Determine Water loss and LOI

Some laboratories use TGA-DSC to determine LOI. A typical curve for a lithium carbonate samples is shown in Figure 2 (after²).

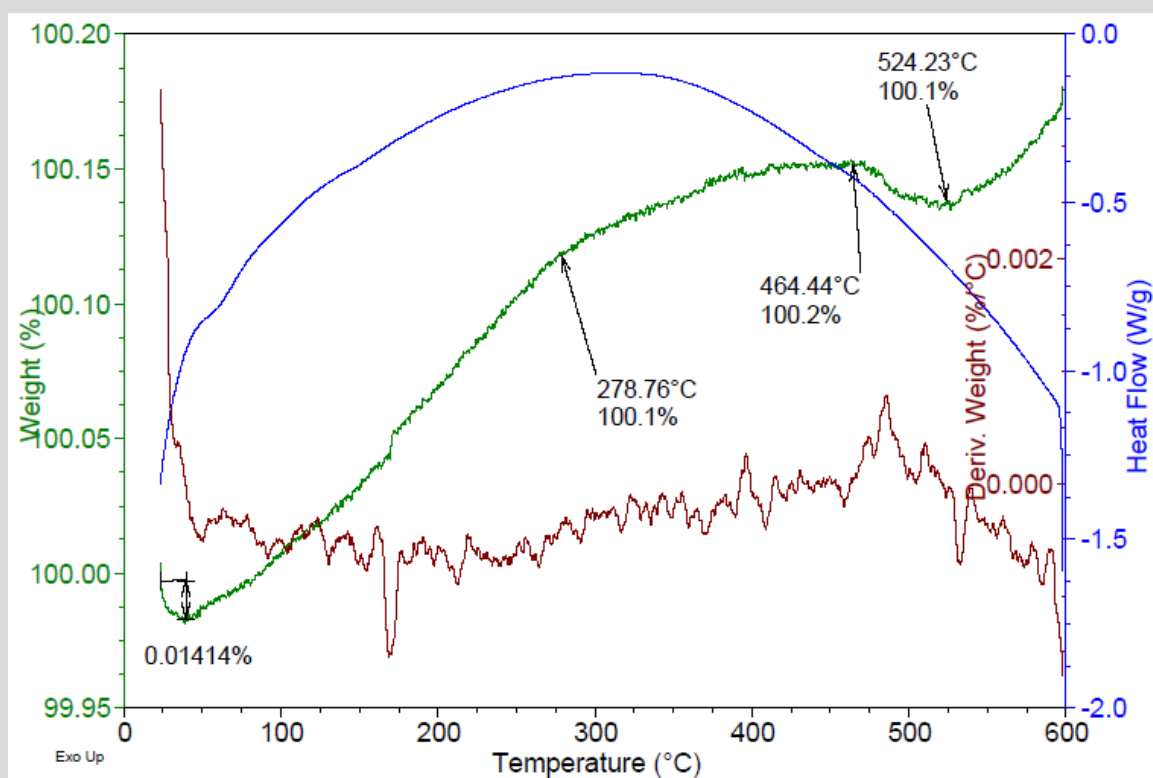


Figure 2: TGA-DSC for a lithium carbonate sample

The TGA-DSC plot in figure 2 suggests:

1. 'LOI' due to physisorbed water <100°C is 0.014% due to being dried at 110°C.
2. 'LOI' due to HCO₃ commences at about at ~280°C and continues down to about 520°C and using this as a basis the estimated mass loss due to HCO₃ is about 0.11%

While this is a convenient way to measure mass loss as a function of temperature, especially for very small samples, the trace is not an equilibrium curve due to the presence of an air stream and a set temperature ramp up. For this reason, placing a sample in the oven at 500°C to achieve constant weight is a more accurate way to determine LOI. However, this requires a larger amount of sample (~10 – 50 g) in order to provide an accurate measure of the mass loss. Further, re-adsorption of water on cooling has to be prevented.

In comparison, TGA-DSC only requires 25-50 mg and can be readily conducted. There are therefore pros and cons for both methods.

Acid Insolubles are solids that do not dissolve when the samples are subjected to dissolution in hydrochloric or nitric acid under defined conditions (temperature, times etc). Usually the amount of acid insoluble is very small and for this reason, the sample size required to do this analysis is probably at least 50 grams. This is typically a problem for the testwork performed as part of feasibility studies where the amount of lithium carbonate produced is far less than 50 grams.

Even a single paper fibre from the filter paper can be enough to overstate the amount of acid insoluble present in the sample. Typically, the acid insoluble content would be less than 0.02 wt% and is considered to be the amount of TOC present in the solids.

Sum of Impurities is usually determined by digesting (dissolving) the sample in either a single or 4 acids and analysing the liquor using an ICP-OES (Inductively Coupled Plasma with optical emission spectrometer). Halides are typically analysed using an Ion Selective Electrode (ISE) technique.

In many cases the purity of the lithium carbonate is determined based on only a small number of possible impurities being analysed. In general, the smaller the number of impurities analysed, the

higher the purity reported. For this reason, it is suggested to analyse for all the elements that are present in the Table 2. These are:

Al, As, B, Ca, Cl, Cr, Cu, F, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, S, Si, Sr, Zn

As a general rule, all elements present in concentrations above 1 g/L in the pregnant liquor prior to lithium carbonate precipitation and bicarbonation should be analysed for in the lithium carbonate solids. The reason for this is that the cation impurity level in the solids is typically 10 – 20 times the concentration in the feed liquor.

It is further suggested that all elements that are below the detection limit only half the detection limit value is deducted as shown in formula 2⁽⁹⁾.

$$\text{Sum of Impurities} = \Sigma (\text{wt\% impurities detected}) + \Sigma (\text{wt\% Detection Limits of impurities NOT detected}) / 2$$

Formula 2

It is typical that the values of the water content and LOI are the largest and the total impurities and acid insolubles far smaller.

LITHIUM CARBONATE PURITY

The second way of reporting lithium carbonate is the purity as shown in the Formula 3. Both the water content and the LOI are not considered to be impurities for battery manufacturers and therefore they are not deducted.

$$\text{Lithium Carbonate Purity} = 100\% - \text{Acid Insolubles} - \text{Sum of the Impurities}$$

Formula 3

Most producers use this formula in reporting high purity, EV grade, lithium carbonate. For a typical battery grade material the value would be > 99.5 wt%.

CALCULATION OF A BATTERY GRADE LITHIUM CARBONATE PURITY AND CONTENT

Two methods are presented in this paper and compared based on the same assumed battery grade lithium carbonate.

The methods are:

1. The Anion and Cation Balance Method, and
2. The Speciation Method.

Cation Anion Balance Method

The calculation is shown in Table 1. In this method the ICP and ISE value for each element are entered as ppm. The method assumes that the elements As, B, Mo, P and Si are all present as anions at the pH normally encountered in precipitation. Specifically, As is present as $(\text{AsO}_4)^{3-}$, B as $(\text{BO}_3)^{3-}$, P as $(\text{PO}_4)^{3-}$, Mo as $(\text{MoO}_4)^{2-}$ and Si as (SiO_2) . (Effectively this is a speciation of the anions). All the other metal elements are present as cations.

The method subtracts the total calculated anionic charge (equivalents) from the total cation equivalents and assumes that the difference is essentially carbonate with a small amount of bicarbonate. [The equivalents are calculated by multiplying the number of moles of each element by the valence of the anion or cation]. (All assays below detection limit were assumed to be at half the detection limit).

Table 1: Cation-Anion Calculation Method of Lithium Carbonate Content and Purity

CATIONS					ANIONS				
Element	ppm	Mol Wt	Valence	Equivalent	Element	ppm	Mol Wt	Valence	Equivalent
Al	2.1	26.98	3	0.133	Cl	29.4	35.45	1	0.829
Ca	5	40.08	2	0.250	F	24.5	19	1	1.289
Cr	1.2	52	6	0.138	SO4	45.6	32.06	2	2.845
Fe	1.2	55.84	2	0.043	HCO3	0.00	61.01	1	0.000
K	21.8	39.1	1	0.558	AsO4	2.23	138.9	3	0.048
Li	185938	6.94	1	26792	BO3	6.53	58.8	3	0.333
Mg	1.2	24.31	2	0.099	PO4	57.0	95	3	1.800
Na	217	22.99	1	9.439	MoO4	0.17	159.9	2	0.002
Cs	0.1	132.91	1	0.001	CO3	804007	60.01	2	26796
Cu	0.2	63.55	2	0.006	TOTAL	804172		TOTAL	26803
Mn	0.1	54.94	2	0.004					
Ni	0.2	58.69	2	0.007					
Pb	0.1	207.2	2	0.001					
Rb	0.1	85.47	1	0.001					
Sr	0.1	87.62	2	0.002					
Zn	0.1	65.38	2	0.003					
TOTAL	186188		TOTAL	26803					

UNCHARGED				
Element	ppm	Mol Wt	Valence	Equivalent
SiO2	13.26	92.1	0	0

Impurities=	0.043 wt%
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Using the Cation Anion Balance Method, the purity of the example lithium carbonate is 99.96 wt% (100% – 0.043%).

This sample had essentially no LOI nor water content. The water content was zero as a result of the drying of the sample and careful storage to prevent reabsorption of water from the atmosphere. The acid insoluble could not be determined due to the amount of sample being too small.

The Speciation Method

Table 2 shows the same bicarbonated battery grade lithium carbonate composition as assumed for the Cation Anion Balance Method. For example, aluminium is <4.2 ppm in both methods. [Only Li, K, Na, S and Cl were above the detection limits for the respective elements].

Table 2: Typical Battery Grade Lithium Carbonate Content and Assumed Speciation

Element	Concentration [ppm]	Assumed Species
Al	<4.2	Al ₂ (CO ₃) ₃
As	<2.4	Na ₃ AsO ₄
B	<2.4	Na ₂ B ₄ O ₇
Ca	<10.0	CaCO ₃
Cr	<2.4	Na ₂ CrO ₄
Fe	<2.4	FeCO ₃
K	21.8	K ₂ CO ₃
Mg	<2.4	MgCO ₃
Na	217.0	Na ₂ CO ₃
P	<37.2	Na ₃ PO ₄
S	15.2	Na ₂ SO ₄
Si	<12.2	SiO ₂
Element	Concentration [ppm]	Assumed Species
Cs	<0.2	Cs ₂ SO ₄
Cu	<0.4	CuCO ₃
Mn	<0.2	MnCO ₃
Mo	<0.2	Na ₂ MoO ₄
Ni	<0.4	NiCO ₃
Pb	<0.2	PbCO ₃
Rb	<0.2	Rb ₂ SO ₄
Sr	<0.2	SrCO ₃
Zn	<0.2	ZnCO ₃
Cl	29.4	NaCl
F	24.5	NaF

In the second step of the calculation the elements are assumed to be speciated as the compounds shown in Table 2. The worked example is shown in Table 3. In the method the split of Na and carbonate is manually adjusted to achieve the overall balance. The method calculates the lithium carbonate purity as 99.94 wt% (100 - 0.06).

COMPARISON BETWEEN METHODS

The impurity content using the Cation Anion Balance Method is 0.054 wt% compared with 0.066 wt% using the ANSTO method.

The main differences between the two methods are:

1. The assumed species.
2. The Speciation Method assumes that elements are present as species shown in Table 2 with the measured sodium content manually distributed between the different forms shown in Table 1. The Cation-Anion Balance Method assumes the forms of the anions but does not make any assumptions on how the carbonate is associated.

In summary, the Cation-Anion Balance Method is quicker to use and calculates a lower value of impurities. The Speciation method is more detailed and assumes part of the carbonates are

associated with impurity species and therefore calculates a higher impurity number. Both assume some speciation and the difference is within the error band for analysis.

CONVERTER BATTERY GRADE SPECIFICATION

The specifications of the main lithium carbonate converters are shown in Table 2. The source of the lithium carbonate for SQM, FMC, Albemarle (Rockwood) and Olaroz is brine, whereas the source for Ganfeng and Tianqi is spodumene. Both Tianqi and Ganfeng state their battery grade lithium carbonate meets the Chinese specifications YS/T582 (2013) for battery grade lithium carbonate.

There is considerable variation between the specifications in table 3. The Olaroz specification is very high and reflects that the product has been bicarbonated (re-crystallised). In general the species of interest are the Group I elements (Na, K and Rb), the halides (F, Cl) and the sulphates. Most cathode producers have advised that the levels of impurities published by the Converters is not a problem but variability from batch to batch is a problem.

In the present market where demand exceeds supply, cathode manufacturers tend to have to buy what is available even if the lithium carbonate contains higher levels of impurities. It is reported that some cathode manufacturers are refining the lithium carbonate in Japan and Korea in order to remove the impurities so the lithium carbonate is suitable for cathode and electrolyte production.

Table 3: Main Lithium Converters Battery Grade Lithium Carbonate specifications⁽⁴⁾⁽⁵⁾⁽⁷⁾⁽⁸⁾

Chemical Properties	SQM Battery Grade (June 21012)	FMC Battery Grade (June 2012)	Olaroz Battery Grade	Rockwood Battery Grade (April 2012)	Ganfeng (Tested)	Tianqi/ Chinese Battery Grade YS/T582-(2013)
Li ₂ CO ₃		99.5	99.5	99.8	99.57	99.5
Na [wt%]	0.06	0.05	0.01	0.065	0.020	0.025
K [wt%]	0.005		0.001	0.001	0.0015	0.001
Ca [wt%]	0.01	0.040	0.01	0.016	0.0031	0.005
Zn [wt%]	0.001	0.0005	0.0005			0.0003
Mg [wt%]	0.01		0.006	0.007	0.0039	0.008
Fe [wt%]	0.001	0.0005	0.0005	0.001	0.0002	0.001
Ni [wt%]	0.001	0.0006	0.0005		0.00029	0.001
Al [wt%]			0.0005		0.0022	0.001
Mn [wt%]			0.001		0.00009	0.0003
Pb [wt%]	0.001		0.0005		0.00013	0.0003
Cu [wt%]	0.001	0.0005	0.0005		0.00012	0.0003
Cr [wt%]	0.001		0.0005			
B [wt%]			0.001			
Si [wt%]			0.001		0.0001	0.003
Cl [wt%]	0.01	0.01	0.005	0.015	0.0017	0.003
SO ₄ [wt%]	0.03	0.1	0.03	0.05	0.066	0.08
F [wt%]						
Moisture Content [wt %]	0.2	0.5	0.2	0.35	0.20	0.25
Acid Insolubles [wt%]	0.01	0.02	0.01			
L.O.I. [wt%]	0.5	0.5	0.5			

CATHODE AND BATTERY MANUFACTURER'S SPECIFICATION

The reality is that there is enormous secrecy amongst the cathode and battery manufacturers in a market where technology is developing at a rapid pace. As such there are no published manufacturer specifications and little information about the deleterious effect of certain impurities on battery performance in the public domain.

A couple of examples are known of cathode and battery manufacturers requiring converters to make modifications to their plant which has included purchasing new equipment. An example was a Japanese battery manufacturer insisting on the installation of a dust free bagging plant in a Chinese Converter's plant. If the lithium carbonate market changes from under-supply to over-supply, then it is foreseeable that cathode and battery manufacturers will be able to impose their internal specification on the lithium carbonate converters, which they are not able to do at present.

BATTERY CONSTRUCTION

There is an increasing number of battery chemistries and construction of Li-ion batteries in the market. Each of these has different fabrication steps which result in an impurity either being a problem or alternatively not being a problem. In this paper a simplistic overview is provided what the impact of impurities is likely to be on a typical Li-ion battery.

Figure 3 shows the typical construction of a spiral wound lithium battery (also called Jelly-roll or Swiss-roll construction).

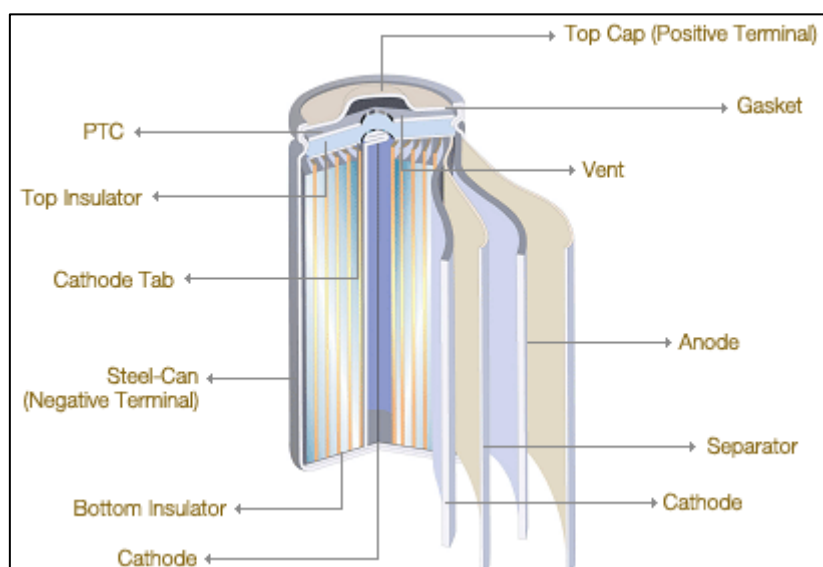


Figure 3: Spiral Wound Cylindrical Cell ⁽³⁾

The construction provides large active surface area of the electrodes by making the electrodes and the separator from long strips of foil and rolling them into a spiral or cylindrical jelly-roll shape. This type of construction has very low internal resistance and is used extensively for lithium-ion secondary batteries.

Lithium ion batteries are constructed in a discharged state which means that all the lithium ions are contained at the cathode and the graphite anode does not contain any lithium. Thus, the batteries need to be charged before use which requires oxidation and reduction reactions to occur at the cathode and anode respectively. During the subsequent discharge process, these reactions are reversed.

A solid electrode interface (SEI) forms during the initial charging and may continue to grow during successive charges. The SEI films acts as an ionic conductor that enables lithium to migrate through the film during intercalation and de-intercalation. At the same time the SEI serves as an inductively passive electronic insulator which prevents further breakdown of electrolyte at the anode.

IMPACT OF IMPURITIES ON BATTERY PERFORMANCE

The more one read about the rapidly developments and different battery chemistries the more difficult it becomes to generalise as to what impurities can cause problems in “all” batteries. In general, one can say:

- Not all impurities pass from the initial cathode material pass through to the finished cathode,
- Some impurities can be converted into insoluble compounds that are electrochemically inactive,
- An impurity in one chemistry is not necessarily a problem in another chemistry,
- An impurity might have a greater impact in the electrolyte than in the cathode, and
- Some impurities are simply harmless spectators.

Issues in battery manufacture and operation include:

Cathode Production

High purity precursors under the correct manufacturing conditions and particle size will produce uniform crystals which have a very high energy capacity. The presence of sodium and potassium can lead to changes to the unit cell and disruption of the crystal lattice.

SEI Growth or Breakdown

Problems can occur if either the SEI film properties change and/or the SEI breaks down. In the case of changes to the SEI these include the film becoming thicker and converting the SEI into an insulating layer rather than an ionic conductor, resulting in battery fade.

Side Reactions in the Electrolyte

Impurities in the electrolyte can lead to corrosion of the battery components. Specifically, the halides impurities if oxidised. While the nature of the corrosion can vary, in general it can lead to the consumption of active chemicals leading to increased impedance and capacity loss.

Transition metals with multiple possible oxidations states undergo easy redox processes commonly between oxidation states 2+ and 3+ which allows these elements to transfer between the anode and cathode and contribute to self-discharge. This would reduce the charge-discharge efficiency.

Short Circuiting

Short circuiting is usually associated with dendrite formation but can also be caused by metal shards in the lithium chemicals which can penetrate the thin separator membrane. For this reason, there is a specification on metal content which would eliminate metal particles large enough to penetrate the membrane.

In Table 5 the common impurities found in lithium carbonate are grouped according to the most likely impact they will have in a Li-ion battery performance.

Table 5: Summary of Expected Impact of Common Impurities on Li-ion Battery Performance

Element	Expect to Impact Li-ion Battery Performance	Comment
Halides: Cl, F and Br	Yes	Potentially powerful oxidisers
Na, K	Yes	Could impact cathode crystal formation
Fe, Co, Ni, Cr	Yes	Redox active metal
Al, Si, Ca and Sr	No	Expected to be stable oxides or other insoluble compounds
SO ₄ , B(OH) ₃	No	Spectators
Other transition metals	No	If soluble likely to plate out on the anode

SUMMARY

Currently there are two main ways to specify lithium carbonate. These are the lithium carbonate content which is typically reported by converters in their product specifications and secondly lithium carbonate purity. Lithium carbonate purity is similar to lithium carbonate content but does not consider the water content and LOI (loss on ignition).

A recommended calculation method is proposed which will make the stated lithium contents and purities comparable between converters and junior miners. Currently this is not possible for several reasons including:

- Different formulae are being used,
- The formula is not stated,
- The number of impurities included in the analysis is different.

In addition, there is no internationally recognised specification but individual specifications from each major converter and a Chinese standard. Cathode and Battery manufacturers do have internal specifications but these are not published. In the current market, where demand exceeds supply, the cathode and battery manufacturers have limited ability to impose their requirements, but there is growing evidence that the manufacturers are assisting converters by insisting on changes to their plants.

Impurities in the lithium carbonate do impact the performance of lithium batteries and while there is a range of cathode chemistries, there are key aspects such as:

- Changing the crystal structure in the cathode,
- Breakdown of the SEI,
- Corrosion of battery components, and
- Short-circuiting

The impurities most likely to affect battery performance are Group 1 elements, halide and redox active transition elements.

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