

23rd Annual Conference Proceedings

Uranium-REE-Lithium Conference

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Lithium Processing Forum



14th Annual Uranium Event

ALTA Metallurgical Services, Melbourne, Australia www.altamet.com.au

PROCEEDINGS OF

ALTA 2018 URANIUM-REE-LITHIUM SESSIONS

Including Lithium Processing Forum

24-25 May 2018 Perth, Australia

ISBN: 978-0-9946425-3-0

ALTA Metallurgical Services Publications

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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.

INTRODUCTION

Even chemists and engineers that have been involved with the lithium industry for a number of years battle to answer the question of "what is battery grade?" The purpose of this paper is to present:

- propose the methods of reporting lithium carbonate purity and content,
- the differing specifications for lithium carbonate, and
- how trace level impurities affect battery manufacture.

Part of the confusion in reporting lithium chemical purity is that most laboratories consider that it is not possible to analyse the lithium carbonate directly to confirm it is battery grade. In order to confirm that the solid purity is >99.5% requires an analytical method with an error far less than 0.05%. This is practically impossible for all the laboratories using ICP (Inductively Coupled Plasma) analysis techniques which typically have an error of around 5%.

The typical detection limits for ICP OES and ICP-MS are shown in Figure 1 (after⁽¹⁾). The advantage of this method is that up to 70 elements can be analysed at the same time and explains why it is the most favoured analytical tool in the analysis of lithium solids and liquors.

The original of the often-quoted figure of 99.5% as battery grade appears to have originated from converters specifications that include a minimum lithium carbonate content. Regrettably there is no simple answer to the question and there are a number of companies that in the absence of an established method of reporting what constitutes battery grade, have claimed to have produced battery grade that would not be regarded as such by most of the industry. In recent years a number of junior lithium explorers have been in print claiming to have produced battery grade with surprisingly little evidence that they are even close. It is hoped that the proposed methods in this paper will provide a consistent reporting level which will increase transparency of information supplied to the industry and investment communities.



Figure 1: Detection Limits of Elements Using ICP-OES and ICP-MS (after¹)

In the following sections the concepts of Lithium Carbonate Content and Lithium Carbonate Purity are discussed and a worked example provided to shown how lithium carbonate can be analysed.

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:

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

<u>Water Content</u> 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:

$2\text{LiHCO}_3 \rightarrow \text{Li}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2$

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 physiosorbed 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 ($\sim 10 - 50$ g) in order to provide an accurate measure of the mass loss. Further, readsorption 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.

<u>Acid Insolubles</u> 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 if 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 preformed 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.

<u>Sum of Impurities</u> 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 $2^{(9)}$.

Sum of Impurities = Σ (wt% impurities detected) + Σ (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.

Lithium Carbonate Purity = 100% - Acid Insolubles - 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 $(AsO_4)^{3-}$, B as $(BO_3)^{3-}$, P as $(PO_4)^{3-}$, Mo as $(MoO_4)^{2-}$ 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

		CATION	S			-	ANIONS	5		
Element	ppm	Mol Wt	Valence	Equivalent	Element	ppm	Mol Wt	Valence	Equivalent	
Al	2.1	26.98	3	0.133	CI	29.4	35.45	1	0.8	
Ca	5	40.08	2	0.250	F	24.5	19	1	1.2	
Cr	1.2	52	6	0.138	SO4	45.6	32.06	2	2.8	
Fe	1.2	55.84	2	0.043	HCO3	0.00	61.01	1	0.0	
К	21.8	39.1	1	0.558	AsO4	2.23	138.9	3	0.0	
Li	185938	6.94	1	26792	BO3	6.53	58.8	3	0.3	
Mg	1.2	24.31	2	0.099	PO4	57.0	95	3	1.8	
Na	217	22.99	1	9.439	MoO4	0.17	159.9	2	0.0	
Cs	0.1	132.91	1	0.001	CO3	804007	60.01	2	267	
Cu	0.2	63.55	2	0.006	TOTAL	804172		TOTAL	268	
Mn	0.1	54.94	2	0.004						
Ni	0.2	58.69	2	0.007						
Pb	0.1	207.2	2	0.001			UNCHARG	ED		
Rb	0.1	85.47	1	0.001	Element	ppm	Mol Wt	Valence	Equivaler	
Sr	0.1	87.62	2	0.002	SiO2	13.26	92.1	0		
Zn	0.1	65.38	2	0.003						
TOTAL	186188		TOTAL	26803	Impuritie	s=	0.043	wt%		

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 Batter	Grade Lithium	Carbonate Content and	Assumed Speciation
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Element	Concentration [ppm]	Assumed Species						
AI	<4.2	Al2(CO3)3						
As	<2.4	Na3AsO4						
В	<2.4	Na2B4O7						
Са	<10.0	CaCO3						
Cr	<2.4	Na2CrO4						
Fe	<2.4	FeCO3						
К	21.8	K2CO3						
Mg	<2.4	MgCO3						
Na	217.0	Na2CO3						
Р	<37.2	Na3PO4						
S	15.2	Na2SO4						
Si	<12.2	SiO2						
F 1	Concentration	Assumed						
Element	[ppm]	Species						
	-0.2	C-2804						
CS Cu	<0.2	US2304						
Cu	.0.4	0002						
N /1.0	<0.4	CuCO3						
Mn	<0.4	CuCO3 MnCO3						
Mn Mo	<0.4 <0.2 <0.2	CuCO3 MnCO3 Na2MoO4						
Mn Mo Ni	<0.4 <0.2 <0.2 <0.4	CuCO3 MnCO3 Na2MoO4 NiCO3						
Mn Mo Ni Pb	<0.4 <0.2 <0.2 <0.4 <0.2	CuCO3 MnCO3 Na2MoO4 NiCO3 PbCO3						
Mn Mo Ni Pb Rb	<0.4 <0.2 <0.2 <0.4 <0.2 <0.2	CuCO3 MnCO3 Na2MoO4 NiCO3 PbCO3 Rb2SO4						
Mn Mo Ni Pb Rb Sr	<0.4 <0.2 <0.2 <0.4 <0.2 <0.2 <0.2 <0.2	CuCO3 MnCO3 Na2MoO4 NiCO3 PbCO3 Rb2SO4 SrCO3						
Mn Mo Ni Pb Rb Sr Zn	<0.4 <0.2 <0.2 <0.4 <0.2 <0.2 <0.2 <0.2 <0.2	CuCO3 MnCO3 Na2MoO4 NiCO3 PbCO3 Rb2SO4 SrCO3 ZnCO3						
Mn Mo Ni Pb Rb Sr Zn Cl	<0.4 <0.2 <0.2 <0.4 <0.2 <0.2 <0.2 <0.2 <0.2 <0.2 29.4	CuCO3 MnCO3 Na2MoO4 NiCO3 PbCO3 PbCO3 Rb2SO4 SrCO3 ZnCO3 NaCl						

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, CI) 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.

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				
AI [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				
CI [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							

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

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.

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

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

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.

ACKNOWLEDGMENTS

The author would like to personally thank Dr Chris Griffith, ANSTO and Dr Stephen la Brooy, Ausenco for their thought provoking comments and contributions that led to the production of this paper.

REFERENCES

- 1. Evans Analytical Group, 2018. "ICP-OES and ICP-MS Detection Limit Guidance", , downloaded from <u>http://www.nanoscience.co.jp/surface_analysis/pdf/icp-oes-ms-detection-limit-guidance-BR023.pdf</u>, 31 March 2018.
- 2. Griffiths, C., 2018. Personal communication.
- 3. Lawson, B., 2018. "Why Batteries Fail", <u>http://www.mpoweruk.com/failure_modes.htm</u> "Lithium Carbonate, Battery Grade", QS-PDS-1059 Revision 1, FMC Lithium
- 4. "Lithium Carbonate, Battery Grade", www.salesdejujuy.com "Lithium Carbonate Battery Grade and battery Grade Low Sodium", Rockwood Lithium, downloaded from www.rockwoodlithium.com/batteries
- 5. "Lithium carbonate high pure grade", Ganfeng Lithium Co., Ltd, <u>http://www.ganfenglithium.com/pro_en/id/45.html</u>, downloaded 2 April 2018.
- 6. The Electropaedia, http://www.mpoweruk.com/cell_construction.htm
- 7. "Tianqi Lithium Corporation -Product Manual", May 2016

- 8. Voelker, P., 2014. "Trace Degradation Analysis of Lithium-Ion Battery Components", R&D Magazine, , April 2014. <u>http://www.rdmag.com/articles/2014/04/trace-degradation-analysis-lithium-ion-battery-components</u>
- 9. Weber, M., Wuthrich, J.,, 2007. "Part 3: Challenges in the characterization of high-purity starting materials", Analytix, 2007, 12-14. https://www.sigmaaldrich.com/content/dam/sigma-aldrich/docs/Sigma/General_Information/analytix_2007_2_p12-14.pdf

Table 5: Speciation Method

Element	Concentration [ppm]	Assumed Species	AI	As	В	С	Ca	Cr	Fe	к	Mg	Na	Ρ	S	Si	Cs	Cu	Mn	Mo	Ni	0	Pb	Rb	Sr	Zn	Cl	F	Species Total [ppm]
Al	2.1	Al2(CO3)3	2.1			1.4															5.60							9.1
As	1.2	Na3AsO4		1.2								1.1									1.03							3.3
В	1.2	Na2B4O7			1.2							1.3									4.14							6.6
Ca	5.0	CaCO3				1.5	5.0														6.00							12.5
Cr	1.2	Na2CrO4						1.2				1.1									1.48							3.7
Fe	1.2	FeCO3				0.3			1.2												1.03							2.5
К	21.8	K2CO3				3.3				21.8											13.38							38.5
Mg	1.2	MgCO3				0.6					1.2										2.37							4.2
Na	217.0	Na2CO3				29.3						112.5									117.34							259.1
Р	18.6	Na3PO4										41.5	18.6								38.45							98.5
S	15.2	Na2SO4										10.8		15.1							30.17							56.1
Si	6.1	SiO2													6.1						6.95							13.0
Cs	0.1	Cs2SO4												0.02		0.1					0.05							0.2
Cu	0.2	CuCO3				0.0											0.2				0.15							0.4
Mn	0.1	MnCO3				0.02												0.1			0.09							0.2
Mo	0.1	Na2MoO4										0.0							0.1		0.07							0.2
Ni	0.2	NiCO3				0.0														0.2	0.16							0.4
Pb	0.1	PbCO3				0.01															0.02	0.1						0.1
Rb	0.1	Rb2SO4												0.04							0.07		0.1					0.2
Sr	0.1	SrCO3				0.01															0.05			0.1				0.2
Zn	0.1	ZnCO3				0.02															0.07				0.1			0.2
Cl	29.4	NaCl										19.1														29.4		48.4
F	24.5	NaF										29.6															24.5	54.1
																								Т	otal Im	puritie	es	612.0
Li	185,938	Li2CO3				159,508															638,033							983,480
	-	•																						Total /	Accoun	tabilit	v	984,092