

Circularity of end-of- life Lithium Batteries: While contributing to the Green Economy may constitute a start for the Non-Dependance of Telecommunication Technology Sourcing Countries

Antoine F. Mulaba – Bafubiandi^{1,2,*}

Abstract—A typical Li-ion-nickel manganese cobalt (NMC), battery is more than 90% composed of about Mn (2%) , Al (5%) , Ni (9%), graphite (10%), Cu (12%), Li (16%, as LCE equivalent), and Co(39%). The observed and more and more predicted increase in the number of recycling efforts leading to the use of green chemistry and the global mushrooming of the LIB recycling plants and sites, would make the lithium battery producers auto sufficient in the required storage energy related metal components. Using a projective analysis of the impact of the circularity of the end-of- life of lithium- ion batteries, this paper rings a bell on either the need for diversification or for new products development from countries naturally endowed with minerals resources termed as energy transition natural resources.

Keywords—Lithium-ion batteries, circularity, green chemistry, diversification, non-dependance, telecommunication industry.

I. INTRODUCTION AND BACKGROUND

Lithium-ion batteries are made of an anode in graphite and lithium metal oxide in the cathode. The currently used systems involve the following: a graphite as anode and a cathode made of lithium metal oxides as lithium-iron phosphate (LFP), lithium nickel cobalt aluminum oxide (NCA lithium-nickel manganese cobalt (NMC), lithium-manganese oxide (LMO), or lithium-titanate oxide (LTO). First generation LIBs mainly used in portable electronics were lithium-cobalt oxide (LCO) bearing.

Circularity as understood in this paper encompasses the “refurbish, reuse, recycle” circular economy principle. It involves the recycling and the re-use for possibly new applications while two or more industries successively

Antoine F. Mulaba-Bafubiandi is with the Mineral Processing and Technology Research Center, Department of Metallurgy, School of Mining Metallurgy and Chemical Engineering, Faculty of Engineering and The Built Environment, University of Johannesburg, POBox 17011 Doornfontein, Johannesburg, 2028, South Africa, Antoinemulaba1@gmail.com, amulaba@uj.ac.za. He is also with the University of Mbuji-Mayi, Faculty of Applied Sciences, Mbuji-Mayi, POBox 225, Mbuji-Mayi, Kasai, Democratic Republic of Congo

working in symbiosis feed into each other as the wastes generated by one industry or upstream process constitute the feed to the other industry or downstream process. The observed recent efforts in developing environmentally adequate batteries recycling processes have been predicted to quadruple. In general, the process involves, Fig. 1., the discharge of the battery from the vehicle or telecommunication device, the manual dismantlement recovery of the polymeric material, to remove the Cu and Al foils and separator, and the hydrometallurgical recycling of lithium bearing components.

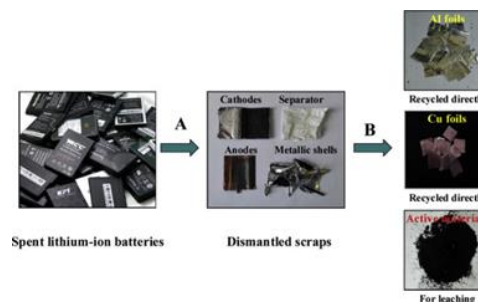


Fig.1. Schematic representation of the dismantling process of the lithium batteries. Adapted from [1]

The development of the LIB recycling industry has led to the enormous increase in the available quantity of LIBs removed from the telecommunication devices as well as used and broken computers, hence reducing the risk of thermal runaway effect causing fires. The lithium battery recycling process which, in 2016 [2] was found not economical [2] has thus surprised the observers by its predicted increase [3].

The extraction of metals content from the used LIB's goes through the dissolution into adequately selected lixivants. Inorganic acids like H_2SO_4 , HCl , HNO_3 , are often used as they provide excellent lixivants with higher metal leaching rates from spent LIBs. Alternative leaching reagents are also taken into consideration due to drawbacks associated with inorganic

acid leaching, such as the creation of hazardous fumes and the handling of caustic acid. The leaching of metals from LIBs was found effective using organic acids due to their biodegradability, effectiveness at high pulp density, and comparatively high leaching efficiency [4]

Therefore, organic acids (such as lactic acid, glucose acid, oxalic acid, and citric acid) started to be employed to recover precious metals. Despite a possible food conflict, the use plants would be suggested as spinach, beets, and other plants are sources of abundant naturally occurring organic acid oxalic acid. This is because a part of the H^+ ion can be ionized by oxalic acid, a kind of strong acid that is present in organic acids. Additionally, because of its potent reducing ability, it can lower the valence of high-valence metal ions and increase the rate at which metals are leached [5]

The lithium metal required in the LIBs may be naturally found in different sources. These include naturally occurring minerals like spodumene, brine and industrial or process effluents. The use of secondary sources will lead to a reduction in the metal extraction from their naturally occurring minerals, Table 1..

Table 1. Natural occurring lithium minerals [3]

Mineral	Formula
Spodumene	$LiAlSi_2O_6$
Holmquistite	$Li_2(MgFe)_2Al_2Si_6O_{22}(OH)_2$
Lepidolite	$K(Li,Al)_2(Si,Al)_4O_{10}(F,OH)_2$
Polyolithionite	$KLi_2AlSi_4O_{10}(F_4OH)_2$
Hectorite	$Na_{0.2}(Mg,Li)_2Si_4O_{10}(OH)_2$
Cookeite	$(LiAl)_2Al_2(AlSi_2O_{10})(OH)_8$
Petalite	$LiAlSi_4O_{10}$
Eucryptite	$Li(AlSiO_4)$
Amblygonite	$(LiNa)Al(PO_4)(F_6OH)$
Lithiophyllite	$LiMn(PO_4)$
Triphyllite	$LiFe(PO_4)$
Elbaite	$Na(Li_2Al_5)Al_4Si_6O_{18}(BO_5)_3(OH)_4$
Jadarite	$NaSiB_2O_2OH$

According to the cobalt and lithium world reserves are represented by Fig.2 and Fig.3 respectively. and the lithium ave

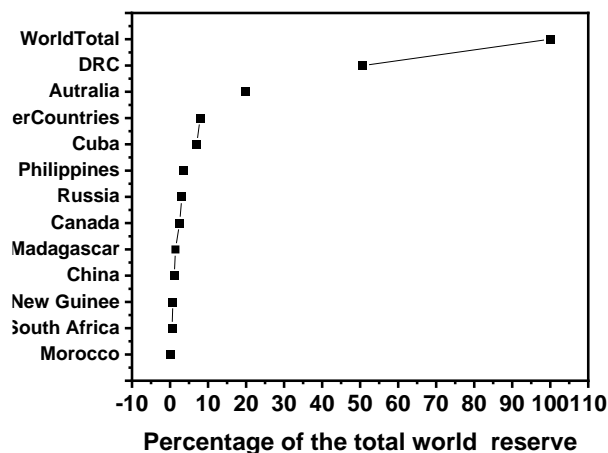


Fig.2. Cobalt world reserve as adapted from [4]. The DRC contains more than 50% of the world cobalt reserve.

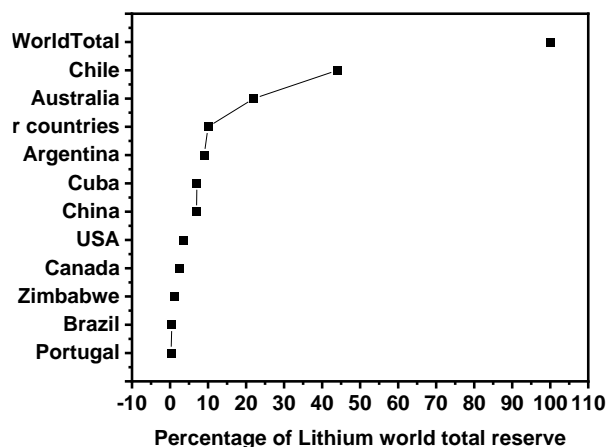


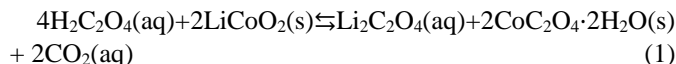
Fig.3. Lithium world reserve as adapted from [4]. Chile contains about 44% of the world cobalt reserve.

II METHODOLOGY

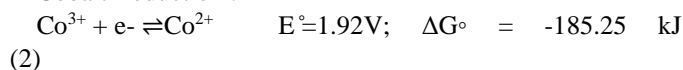
Secondary data were used for the economics study while The positivist research philosophy [6] was used as laboratory experimental tests were conducted to collect primary data and make prediction. It was supplemented by deduction approach. Mono-method quantitative design was used to obtain experimental data. Cross-sectional time was chosen as the research method. X-Ray Diffraction (XRD) was used to identify different crystallized phases on solid sample materials. To determine the various phases that were present in relation to the ICP-OES data, a Rigaku Ultimal V X-Ray Diffractometer fitted with the PDXL software analysis and a copper cathode source $K\alpha=1.78$ was employed. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) was utilized for very small content and trace elements The

hydrometallurgy dissolution of LIB component was carried in

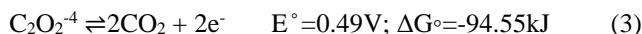
The leaching was conducted in oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) leveraging on its environment friendliness and relatively higher dissolution rate. For the dissolution in oxalic acid of Li and Co containing compounds, the following reactions were considered:



Cobalt Reduction :



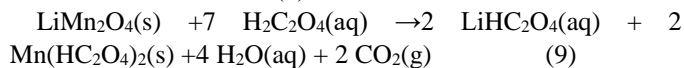
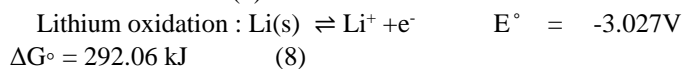
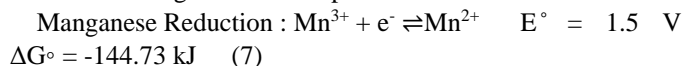
Oxalate Oxidation :



In equation (1), Li and Co are divided into aqueous ($\text{Li}_2\text{C}_2\text{O}_4$) and solid phases ($\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), respectively, illustrates the digestion of LiCoO_2 with aqueous $\text{H}_2\text{C}_2\text{O}_4$ [5](Verma, et al., 2020).

This selective lithium recovery technique can be extended to additional cathode materials, such a Lithium-Nickel-Manganese-Cobalt-Oxide (NMC) batteries with varying metal ratios, LiMnO_2 , and $\text{LiCo}_0.95\text{Mn}_0.05\text{O}_2$ [7](Fung, et al., 2019). This proposed technique can also be applied in the $\text{H}_2\text{C}_2\text{O}_4$ leaching of LiMnO_2 material from coin or button cells.

The following reaction is represented below:



The decision on the choice of selecting the oxalic acid was based on the products that it emits when it is reacted with LiMnO_2 with the off gases (eco-friendly gases) not being too harmful as compared to the gases released by the inorganic lixivants (toxic gases) and its availability of the laboratory (meaning that there will be no time spent in ordering the lixiviant).

II. MATERIALS AND METHODS

The mineralogical study of the material was conducted using X-Ray Diffraction (XRD) for determination of mineral composition. Spent lithium button batteries were used in this study. The batteries were dismantled using pillars, mortars and the steel casings were removed. An *aqua regia* solution (HNO_3 : HCl = 1:3, v/v) was used to digest one gram of lithium-ion battery at 80 °C until practically dry. The concentration of each metal element was determined using

ICP-OES. The solution was then diluted with de-ionized water to a consistent volume. The battery's stainless steel metallic case was stored for later recycling. For the dissolution of the cathodic material (LiMnO_2), the sample material was leached according to the design of experiments conditions (see Table 2) where leaching parameters such as time, S/L ratio were kept constant at 45 minutes and 20% solids, respectively. The pregnant liquor was then filtered to separate soluble $\text{Li}_2\text{C}_2\text{O}_4$ and precipitated MnC_2O_4 . The dissolution of metals from the cathode (lithium and manganese) was predicted through the Pourbaix diagrams (Eh-pH diagrams), Fig. 4 and Fig.5, generated with the software HSC chemistry (version 6).

III. FINDINGS AND DISCUSSION

Using the characterization from the previous section and a S/L ratio of 1g of lithium cathode powder in a volume of 60 ml of the *aqua regia* solution, Pourbaix diagrams were created assuming complete digestion of metals. From the Pourbaix diagram, Fig. 5, the manganese precipitates when the solution potential (E vs pH) is greater than -3.027V in order to accomplish total lithium dissolution. Otherwise, the mechanism of dissolution is not thermodynamically feasible.

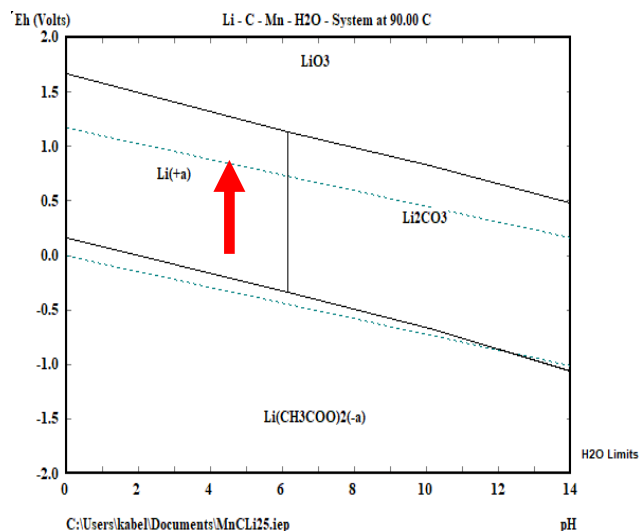


Fig.4. Li-C-H₂O system at 363K.

Table 2 displays the results; the spent LiBs contain a very high concentration of

Therefore this confirms that the LIBs that were used for this study were LiMn_2O_4 coin cells.

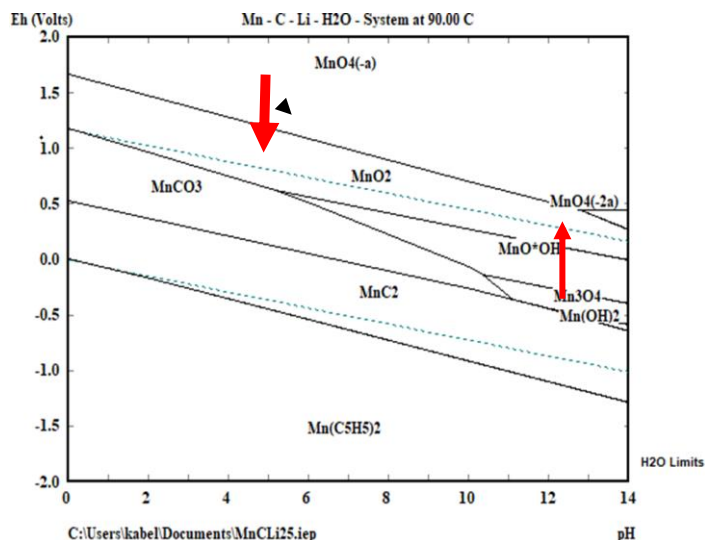


Fig . Mn-C-H₂O system at 363K.

Digestion findings

The digestion of crushed electrode in *aqua regia*, Fig.5 , shows , Table 2, Mn (12810.98mg/l) and minor amounts of Li (1157.71 mg/l) and trace amounts of Co (<0.00 mg/l).



Fig 6. Solution generated from the digestion of the electrode materials in *aqua regia*.

Table 2. ICP-OES results of Li ad Mn content.

Metal	Concentration (mg/L)
Lithium	1157.71
Manganese	12810.98
Cobalt	< 0.01

The XRD pattern of the cathodic material , Fig.7. displays the expected peaks for LiMn₂O₄. at 2θ angles of 25.2° and 67.3°. The identification by ICP-EOS of Li and Mn coupled to

the XRD analysis, in accordance with [7] and leads to confirm that the spent battery is a LiMnCo battery.

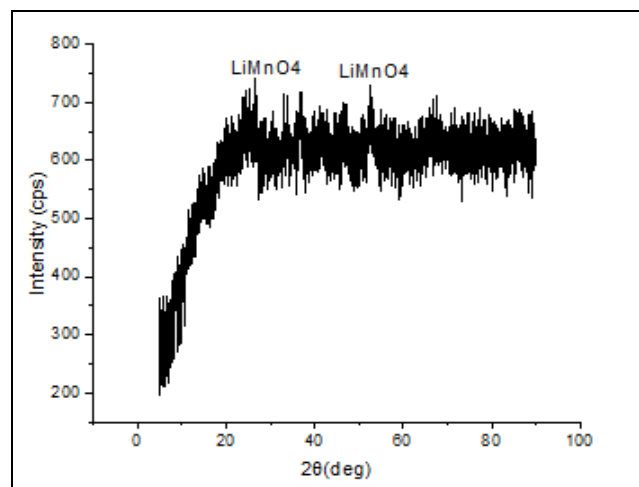


Fig. 7.XRD pattern of electrode material.

Dissolution in oxalic acid

The dissolution in oxalic acid shows, with a contact time of 45 minutes, 1.25M and 60°C an optimum lithium and manganese yield of 48,42% and 4,95%, respectively. The use of reducing or oxidizing agent would improve the expected yield. As recommended by [8], who got in sulfuric acid (1.25M, 60 minutes and at the temperature of 60°C) as a lixiviant and without adding an oxidant, a 93% lithium recovery with 13.3% for manganese.

[9] used the ascorbic acid to recover lithium and cobalt from the spent LIBs. They reported a 94.8 and 98.5% recovery of Co and Li respectively. The leaching was conducted at agitation of 300 rpm in 50 minutes at the acid concentration between 0.3-1.5M and at the temperature of 30-90°C.

This has been proven to be correct because from the leaching experiment results given in Table 2, it has been shown that the residue has high % recoveries of manganese in comparison to the % recoveries of manganese in the leachates. The highest % recovery of manganese in residue was found to be 90,21% where the leaching conditions were 2M and 90°C. Another approach of recovering lithium and manganese has been proposed by [10] by using slurry electrolysis.. They found that the highest percentage of Li₂CO₃ was found to be 99.59% and the MnO₂ was 92.33%. This approach avoids the use of both an oxidant and a reductant because of their toxicity into the environment.

Varying the concentration of the oxalic acid: Effect on the dissolution yield

It was noticed that as the lixiviant concentration increased, the Li recovery % increased during the dissolution of the LIBs (48.42% Li recovery % as the highest. But as the oxalic acid exceeded 1.25M, there was a decrease in the Li recovery % (34.22% Li recovery % being the lowest at 2M). This could be caused by a passivation process.

Effect of temperature

The effect of varying temperature on the oxalic acid dissolution yield was investigated. It was noticed that As the leaching temperature increased, the Li recovery % increased.. The 48.42% Li recovery % was found to be the optimum recovery in the leachate and the leaching temperature was 90°C. According to the findings shown, at 65°C, 82% of Li and 42.6% of Co were leached off. Li and Co recovered at 75°C with rates of 99.1% and 70.0%, respectively. The analysis of variance (ANOVA) was conducted The interaction between the temperature and the acid concentration was observed to be insignificant with respect to recovery of lithium.

Economic analysis

The increasing demand of electric vehicles leads to the same trend demand for electric batteries. The increased demands of electric batteries leads to the increased demand of related electric storage minerals. The case of lithium manganese cobalt lithium batteries was considered in this paper. The development of new technologies for the recycling of used batteries leads to an efficient recovery of lithium components from the end-of -life batteries. As the observed trend is that the countries endowed with energy storage minerals as shown in Fig 2 and Fig. 3 are, for many, the less technology developed countries and as their national gross product is minerals trading dependent, any decline of the mineral trading revenue accrued will negatively affect the GDP of those countries.. On the other hand, the development of green technologies leading to more efficient metals' sensitive to energy transition, will produce sufficient energy metals as required by the energy storage devices, hence the technology developed country will no longer depend on mineral producing countries for the supply of the energy transition minerals.. Hence the development of circularity leads to the non-dependance of technology developed countries vis a vis to minerals endowed countries. Hence, it is advised that the latter either develop their own technologies or diversify the sources of their GDP's revenue.

IV. CONCLUSION

The development of performing recycling and re-use technologies through the concept of circularity as applied to the end- of- life energy storage batteries has been found posing a threat to the GDP contributions of the minerals endowed countries reposing their economy on the minerals trade. A diversification of revenue generation income of such countries is strongly recommended.

Contribution of authors

Antoine F. Mulaba - Bafubiandi initiated, conceptualized, and wrote the paper.

Declaration of interest

The author has no financial nor personal interest in the content of the work here presented.

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