Battery materials research conducted at Mintek towards energy storage and resource efficiency

B. Xakalashe, E. Muller, X. Goso, G. Tawane, S. Nkosi, S. Tsebe, U. Hall, E. Matinde, S. Mokoena, R. Hassanalizadeh, P. Doubra, F. Jantjies, N. Mhlanga, C. Mokwana, M. Raphulu, M. Gericke, and R.F. Sandenbergh

Mintek, South Africa

Given the vast resources of battery materials in Southern Africa, Mintek is undertaking battery materials research across a number of disciplines including hydrometallurgy, pyrometallurgy, advanced materials, mining and mineral economics. In a region with a large extractive metallurgy industry, there is potential for Southern Africa to be a significant player in the battery materials value chain towards energy storage. Utilisation of secondary resources for the recovery of battery materials is also explored. The paper provides a summary of the battery materials-based research projects at Mintek.

Keywords: Battery materials, energy storage, battery precursor materials, battery recycling, Li-ion batteries

INTRODUCTION

South Africa is in a critical state in terms of securing a sustainable and reliable energy supply. The latest load shedding issues have deemed the study into sustainable renewable energy worth investigating. In the transition to renewable energy and e-mobility, energy storage is becoming increasingly important. Batteries, in different shapes and sizes, are key in the energy storage arena. Southern Africa is endowed with a number of primary resources used in battery materials. Mintek, the South African science council on mineral technology, is a leading provider of minerals processing and metallurgical engineering products and services to industry. Mintek is strategically undertaking battery materials research across a number of disciplines including hydrometallurgy, pyrometallurgy, advanced materials and mining and mineral economics. The paper gives a summary of Mintek's expertise in the battery materials research across the aforementioned disciplines.

Hydrometallurgical based research on battery materials

Hydrometallurgical processing of manganese, nickel and cobalt for the production of battery precursor materials

Battery metals are characterised by the low levels of impurities contained in the final product (Huang *et al.,* 2020). That is to avoid unnecessary side reactions which could affect the conductivity and structural stability of the battery and reduce its life span (Nasser and Petranikova, 2021). As reported, the electrode material plays a major role in identification of the electrochemical property for lithium-ion batteries (LIBs) (Peng *et al*., 2019) where the presence of copper leads to a high median voltage, low cyclic stability and low specific capacity (Nasser and Petranikova, 2020). For anode materials, on the other hand, it is desirable for the pure metals to be used, enabling it to efficiently serve its purpose of holding the active ions in a high energy state (Borah *et al*., 2020). The low impurity requirement for these metals is the major contributor to their high cost (Peek *et al*., 2009; Ahmed *et al*., 2017). More processing steps are used to achieve the product specification for battery metals. The number of process steps is also dictated by the processes that are implemented to recover the metal of interest from the host rock or concentrate.

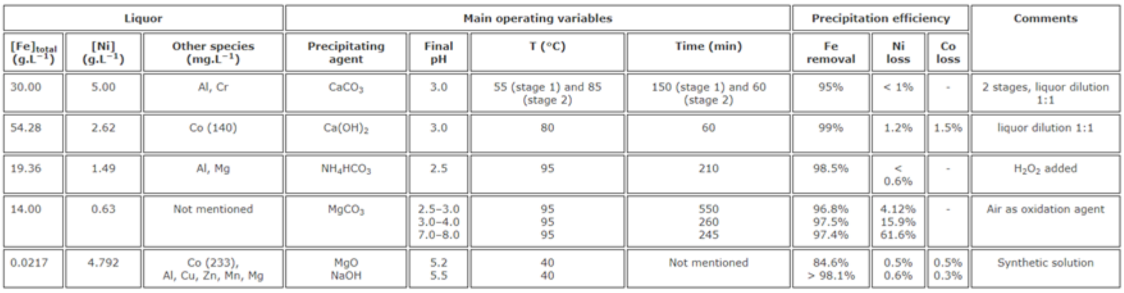
The most common impurity species found in the processing of battery precursor metals such as manganese, cobalt and nickel include iron, aluminium, silica, calcium, chromium, magnesium, calcium, potassium and sodium (Dzyazko and Belyakov, 2004; At-Thyabat *et al.,* 2013; Sole and Cole, 2001). The extent of contamination of these minerals varies from ore to ore and also depends on the processes that are used in the extraction of the metal of interest (Crundwell *et al*., 2011).

In hydrometallurgical purification processes, the purification of the battery precursor metals is done utilising a combination of various techniques including precipitation, ion exchange, solvent extraction and electrowinning (Crundwell *et al*., 2011). Precipitation is mainly used for elements present in higher concentrations (i.e. >500 ppm) and that can be utilised to selectively separate it from the metal of interest, either by pH or other unique properties (Lewis, 2010), in which hydroxide and sulphide precipitation methods are popular; while the lower solubility of metal sulphides, selective metal removal, quick reaction rates, and better settling properties offers advantages over the hydroxide precipitation technique (Zhang *et al*., 2020). Ion exchange is applied mainly for impurities below 500 ppm using suitable resins (Judge and Azimi, 2020).

Decades of research and development studies on solvent extraction of nickel, cobalt and manganese from different ore types have demonstrated it as one of the most efficient technologies in selectively extracting the metal of interest from the complex matrices using suitable organic or extracting impurities from solution (Crundwell *et al*., 2011) and has found interest because of its fast kinetics, cost efficiency and high selectivity for metals resulting in high purity products though the environmental issues still exist (Coll *et al.,* 2012). Further complications due to co-existence of cobalt and nickel along with some other metals have been tackled, and from the long list of acidic, basic and ionic liquid based solvents tested, Cyanex 272 is recommended to separate cobalt and nickel after a manganese removal stage using D2EHPA (Liu *et al*., 2019).

Iron and aluminium are often the dominant impurity elements in battery metals production. Neutralisation is the most common process for removing these metals via an alkaline reagent such as limestone or lime (de Fatima da Silva *et al.,* 2022), a process developed mainly for zinc hydrometallurgical industries. Conditions for the precipitation of metal ions from sulfate solutions are influenced by their relative concentrations and ionic strength (Yue *et al.,* 2016). Neutralisation of the iron containing solution to pH values between 2.5 and 4 should be sufficient to remove all the ferrous iron. However, ferric iron will remain in solution unless an oxidising reagent is added to trigger the generation of ferrous iron (Shen *et al*., 2013). A summary of iron precipitation from sulfuric liquors containing nickel (and other metal species) under varying conditions is presented in Table 1. Aluminium, chromium and silica are also removed with iron during the neutralisation process, however, a slightly higher pH (~4.5) is required for complete removal of aluminium.

Table I. Precipitation of iron from sulfuric liquors containing nickel (and other metal species) under varying conditions (de Fatima da Silva et al., 2022)



Liquor			Main operating variables				Precipitation efficiency			Comments
$[Fe]_{total}$ ($g.L^{-1}$)	[Ni] ($g.L^{-1}$)	Other species ($mg.L^{-1}$)	Precipitating agent	Final pH	T (°C)	Time (min)	Fe removal	Ni loss	Co loss	
30.00	5.00	Al, Cr	$CaCO_3$	3.0	55 (stage 1) and 85 (stage 2)	150 (stage 1) and 60 (stage 2)	95%	< 1%	-	2 stages, liquor dilution 1:1
54.28	2.62	Co (140)	$Ca(OH)_2$	3.0	80	60	99%	1.2%	1.5%	liquor dilution 1:1
19.36	1.49	Al, Mg	NH_4HCO_3	2.5	95	210	98.5%	< 0.6%	-	H_2O_2 added
14.00	0.63	Not mentioned	$MgCO_3$	2.5–3.0 3.0–4.0 7.0–8.0	95 95 95	550 260 245	96.8% 97.5% 97.4%	4.12% 15.9% 61.6%	-	Air as oxidation agent
0.0217	4.792	Co (233), Al, Cu, Zn, Mn, Mg	MgO NaOH	5.2 5.5	40 40	Not mentioned	84.6% > 98.1%	0.5% 0.6%	0.5% 0.3%	Synthetic solution

Other impurities that are found in battery metals production are the alkali metals and the alkali earth metals. The alkali metals are highly soluble and are not expected to contaminate the final product unless they are present in considerable concentrations. If the latter exists, there are options to precipitate sodium and/or potassium as jarosite ($MFe_3(SO_4)_2(OH)_6$ where M is either Na^+, K^+, Ru^+ or NH^{4+}) (Dutrizac, 1983) or to use the membrane technique (Aguilar, 2008). There are also options to remove calcium and magnesium using ion exchange technique or by precipitation using fluorinated reagents.

As one last stage to complement the high grade metal production process, electrowinning is utilised to produce high grade metal. Low current efficiency and high cell voltage are unique technical features of commercial manganese production (Gamali and Vorozhko, 1981) which necessitate a meticulous understanding of process parameters and additives required (Harris *et al.,* 1977). These operating parameters involve hydrogen evolution reaction and its counter effects on manganese plating, polarisation behaviours (Lu *et al.*, 2014), its performance with respect to various additives and finally the plating in the presence of high impurities contents (Biswal *et al.*, 2013). Manganese dissolution after plating is among the most challenging issues that are influenced by impurity content and consequent electrochemical interactions generated via galvanic micro-cells (Shvab, 1972), the thermodynamics of the solution and plating time (Zosimovich, 1967). In the process of Cobalt electrowinning, on the other hand, fewer complications are anticipated and a high grade metal can be plated, provided the correct range of parameters are maintained (Sharma *et al.,* 2005). All the technologies mentioned above are at the technology readiness level levels (TRL) 1-5 and implemented in various locations worldwide. Furthermore, Mintek has developed a synergistic solvent as a combination of pyridine carboxylate and Versatic 10 with the trademark NickSyn. The extensive piloting on various synthetic and industrial pregnant leach solutions (PLSs) have demonstrated its economic viability (Du Preez and Preston, 2004; Masiiwa *et al.*, 2008) while it is yet to be commercialised.

Processing of vanadium for VRFBs

Vanadium is one of the hardest metals, this coupled with its corrosion-resistant nature positions it well for the production of wear-resistant and high-speed tool steels ((Lee, *et al.,* 2021; Yuan, *et al.,* 2021; Roskill, 2010; Mitchell, 2000). To a lesser extent, vanadium is used in the chemical and catalysis industries (Roskill, 2010). In the recent past, vanadium has gained popularity in the energy storage sector for use as a vanadium electrolyte for the production of vanadium redox flow batteries (VRFBs). Amongst the flow batteries in commercial operation, the VRFB is the simplest and most developed. The increased growth of the commercialisation of VRFBs has led to the increased demand for vanadium. The global production of vanadium was in excess of 100 000 tonnes in 2019 (Gao, *et al.*, 2022) It has been projected that the vanadium demand for the production of VRFBs will increase the global vanadium demand by an additional 6% per annum through to 2029. The long-term growth of vanadium demand in the energy storage sector is estimated to be even greater (Bushveld Minerals, 2022).

Given the critical application of vanadium in the energy storage sector, it is important to ensure sustainability in vanadium and VRFB production. In 2021, about 90% of global vanadium production was generated from titaniferous magnetite (titanomagnetite) resources, with only about 10% of the vanadium production generated from secondary resources like fly ash, petroleum residues, alumina slag, and spent catalysts (Bushveld Minerals, 2022). In South Africa, vanadium has primarily been produced from titanomagnetite resources. Thus Mintek has conducted extensive research and development work for the extraction of vanadium from titanomagnetite resources (Tawane, *et al.*, 2021; Lekobotja, *et al.*, 2017; Nkosi, *et al.*, 2017; Goso, *et al.*, 2016; Steele & Wilson, 1966). Vanadium extraction from titanomagnetite is commercially extracted through either the vanadium and steel co-production or vanadium primary production processes (Bushveld Minerals, 2022; Roskill, 2010).

The vanadium and steel co-production process is essentially a pyrometallurgical process that involves the smelting of titanomagnetite in electric arc or blast furnaces (EAF or BF) to produce a vanadium-bearing pig iron and titaniferous slag by-product. The vanadium-bearing pig iron is processed further to co-produce vanadium products and steel. In 2021, the co-production process accounted for about 73% of global vanadium production from titanomagnetite resources. In South Africa, the co-production process was operated by EVRAZ Highveld Steel and Vanadium Corporation (EHSV) (Steinberg, *et al.*, 2011; Taylor, *et al.*, 2006; Moskalyk & Alfantazi, 2003), which became unprofitable and subsequently closed down in 2015. The closure of this operation resulted in a significant drop in vanadium production capacity in South Africa. Hence Mintek is currently involved in extensive research and development work to investigate alternative pyrometallurgical approaches for maximum and efficient exploitation of the titanomagnetite resources and by-products from historical operations (Tawane, *et al.*, 2021; Lekobotja, *et al.*, 2017).

In 2019, the vanadium production from the primary process accounted for about 18% of the global vanadium production (Gao *et al.*, 2022). This process is essentially a roast-leach process, which involves the roasting of titanomagnetite in the presence of a Na reagent to convert V to the water-soluble sodium metavanadate ($NaVO_3$), leaching vanadium using water as lixiviant, and precipitation of vanadium from the PLS (Goso, *et al.*, 2016). South Africa is home to two companies out of the three global commercial vanadium primary production operations around the world, namely; Glencore's Rhovan and Busveld Minerals' Vametco and Vanchem operations. Mintek has been involved in many research activities for the intensification of current operations (Nkosi, *et al.*, 2017; Goso, *et al.*, 2016) as well as supporting start-up operations (Vanadium Resources Limited, 2020).

In summary, Mintek has extensive research and development capacity for the extraction of vanadium from titanomagnetite and secondary resources using vanadium and steel coproduction and vanadium primary production processes. Mintek equipment can be utilised to conduct laboratory and pilot investigations for vanadium extraction following the two commercial process routes. Mintek has clients around the world including in Norway, Italy and South Africa. A number of vanadium extraction projects are currently underway at Mintek, some of which are contracted by commercial clients and the rest being funded by the South African government.

The following subsections provide descriptive summaries of some of the government funded projects that are currently underway at Mintek for the expansion of the vanadium industry in South Africa, and development of human capital for the sustainability of the industry. Some of the projects deal with the valorisation of titaniferous slag produced as the by-product during the vanadium and steel co-production process. Titaniferous slags produced from the South African vanadium bearing titanomagnetite typically contain high vanadium concentrations of about 0.9% vanadium pentoxide (V_2O_5) (Steinberg, et al., 2011). The vanadium concentration in the South African titaniferous slag is multiple-fold higher than that contained in some major vanadium bearing titanomagnetite resources processed around the world. There is about 50 million tonnes of the South African titaniferous slag dump left behind by the now-defunct EHSV. This slag is sitting above ground near the town of eMalahleni and requires no mining.

Titanium and vanadium extraction from titaniferous slag using the sulfation roasting process

The objective of the project is to investigate the best balance of roasting and leaching conditions for maximum extraction of vanadium and titanium products from the discard titaniferous slag, Using the EHSV slag as a case study. The hypothesis is that sulfation roasting of titaniferous slag will convert vanadium in the slag to a water-soluble vanadium oxy-sulfate or vanadyl sulfate ($VOSO_4$), in accordance to equation 1 and decomposition of the complex structure to allow for the upgrading of the residue to a titania feedstock.

$$V_2O_5(s) + 2SO_2(g) + 0.5O_2(g) \rightarrow 2VOSO_4\ (s) \qquad [1]$$

The proposed approach is selective for the sulfation of vanadium under the conditions where impure sulfates are thermodynamically unstable.. The roasted solids are subjected to water leaching to dissolve vanadium. The high purity vanadium PLS is investigated for use as a precursor for the production of vanadium electrolyte for producing VRFBs. The leach residue is also investigated for upgrading using acid and caustic leaching stages to produce a titania feedstock for the production of titania pigment.

Vanadium and titanium extraction from titaniferous slag using a modified vanadium primary production process
The objective of the current project is to investigate the technical feasibility of extracting vanadium (and titanium) from titaniferous slag using a modified vanadium primary production process, which is essentially a roast-leach process. The approach of the current study involves adding sufficient amount of Na reagents for the decomposition of the complex vanadium-bearing mineral composition of the slag such as spinel and pseudobrookite as well as conversion of the vanadium in the slag to the water-soluble $NaVO_3$. The scope of the current project includes the investigations of the optimum composition and amount of $NaCl\text{-}NaOH\text{-}Na_2CO_3\text{-}Na_2SO_4\text{-}Na_2B_4O_7$ reagent for effective decomposition of the slag structure and vanadium extraction using water as lixiviant. The decomposition of the slag also facilitates the beneficiation of the water leach residue through sequential acid and caustic leaching stages for the production of a titania feedstock for the pigment production industry.

Cost effective production of vanadium electrolyte for VRFBs
V_2O_5 is an important by-product that is typically used as a precursor for the production of vanadium electrolyte. Mintek has the technical capacity for the research, development, and support of the industrial vanadium primary production flowsheets for producing V_2O_5 (Goso, 2016). The dissolution of the V_2O_5 material to produce the vanadium electrolyte is challenging, especially when using sulfuric acid or water as the lixiviant. The current project involves an investigation of flowsheets for the production of a vanadium electrolyte from another precursor, other than V_2O_5. The current investigation involves the synthesis of a vanadium electrolyte from the aqueous solution of ammonium metavanadate (AMV), followed by purification of vanadium solution using either solvent extraction or ion exchange.

Exploration of different resins and organics to selectively extract vanadium from the leachate or dissolved AMV solution will assist in the successful confirmation of the hydrometallurgical flowsheet for the production of vanadium electrolyte.

Recovery of lithium from spodumene ore
Since 2016, there has been a significant global demand for minerals used in green energy production, in particular lithium (Muller, 2021). Li minerals include spodumene ($LiAlSi_2O_6$), eucryptite ($LiAlSiO_4$), petalite ($LiAlSi_4O_{10}$), and bikitaite ($LiAlSi_2O_6 \cdot H_2O$), among others. Amongst all of these, spodumene is the primary source of lithium that occurs in pegmatite minerals (Karrech *et al.*, 2020). Moreover, spodumene is the principal commercial hard rock of lithium (Salakjani *et al.*, 2019). Mintek conducted a study on a spodumene-hosted pegmatite. The broad objective of this study was to evaluate the effect of physical beneficiation, thermal pre-treatment, and acid digestion on the recovery of lithium from a spodumene-hosted pegmatite. A spodumene tailings sample was used for this study.

A concentration of 6.78% Li_2O was reported in this study which represents a very promising result given that Li_2O in pure spodumene is 8%. Furthermore, the test work confirmed that for the recovery of lithium from α-spodumene, prior phase conversion to β-spodumene is essential. The project is currently at TRL 2 and ongoing with the focus being the purification of the lithium PLS.

Pyrometallurgical based research on battery materials

Zinc carbon battery recycling in a DC arc furnace

The pyrometallurgy discipline at Mintek is well known for the R&D as well as technology transfer of the direct current (DC) arc furnace technology. The technology has been applied for producing both metal and slag from primary and secondary resources. The technology has been demonstrated in a number of industries including but not limited to the ferroalloys, platinum group metals, rare earth elements, magnesium, ilmenite smelting, and the treatment of various secondary streams. One such a stream is the treatment of pre-processed zinc carbon batteries for the production of ferromanganese and the recovery of fumed zinc. This development was based on Mintek's ENVIROPLAS process for the treatment of solid wastes from the metallurgical industry that contain zinc oxide. The process is based on the carbothermic reduction of selected metal oxides (e.g. zinc oxide) at high temperatures in a DC arc furnace.

Secondary lead smelting in top blown rotary furnace

Recovery of metal values from secondary resources is one of the key focus areas of research in Mintek's pyrometallurgy discipline. Pyrometallurgy is the traditional processing technology to recover lead from end-of-life lead-acid batteries, enabling up to 98% of the lead-acid battery to be recycled (Ballantyne *et al.*, 2018). Despite its success, there are still a number of drawbacks with the pyrometallurgical lead recycling process, primarily related to operational and environmental concerns (Li *et al.*, 2016).

There is a growing need to develop novel processes to recover lead from end-of-life lead-acid batteries, due to increasing energy costs and significant carbon dioxide emissions (Ballantyne *et al.*, 2018). The pyrometallurgy discipline supports the recycling industry by being actively involved in research; exploring alternative reductants (e.g., hydrogen and aluminium) to decarbonise high temperature recycling processes and the use of cheaper energy sources with less carbon dioxide emissions. This includes development of piloting facilities incorporating the utilisation of natural gas as a fuel for powering the lance of a top blown rotary furnace (TBRF). A TBRF is one of the conventional units widely applied in the recycling of lead-acid batteries, and Mintek has completed feasibility studies, in support of industry, and developed expertise in the operation of TBRFs and recycling of lead and other electrical and electronic waste (e-waste).

Pyrometallurgical treatment of spent lithium ion batteries to recover valuable materials

South Africa faces multiple challenges in waste management such as complexity of waste streams and lack of recycling infrastructure, which means that the value of the waste generated in South Africa cannot be effectively reclaimed. The revised National Waste Management Strategy (DEFF, 2020) is centred on the concept of a circular economy to address the problems and opportunities within the waste sector and one of the techniques that can be applied is waste valorisation. Waste valorisation is a process that converts waste material into useful products such as fuels, chemicals and materials (Arancon, 2013). It aims to reuse, recycle or compost waste to produce useful products and sources of energy.

Mintek undertook a study to identify possible waste streams that could be sent for pyrometallurgical treatment to recover valuable metals. The market trends for the generation of the waste stream along with the utilisation of the recovered metal was investigated to determine a possible economically viable option. It was determined that treating spent lithium ion batteries (LIBs) would be the most feasible as it is a waste stream and production stream that would continue to grow in the future mainly due to the increase in electric vehicle (EV) adoption (Harper, *et al.*, 2019). Pyrometallurgical treatment of spent LIB generally focusses on the recovery of cobalt with the possibility of lithium also being recovered (Huang, *et al.*, 2018); however these processes tend to be energy intensive and have to be operated in a specific manner to make them economically viable. The favoured process is to smelt the spent LIB stream in an electric arc furnace to recover an alloy that is sent for further hydrometallurgical refinement as minimal pre-treatment is required (Makuza, *et al.*, 2021). The opportunity exists to investigate specific fluxing regimes to recover a larger percentage of the lithium (which is generally lost to the slag) in the alloy and this will be the focus of future research. This study is at TRL 1 and the work is ongoing.

Advanced materials-based research on battery materials

Carbon nanotubes application for lithium-ion battery anodes

Rechargeable LIBs have emerged as the most promising battery storage technology. The main attributes of LIBs are their long cycle life, high power density, high gravimetric energy, high volumetric energy, and low self-discharge property (Goriparti *et al.*, 2014). More research is however still being conducted to improve the qualities of LIBs, in particular concerning their capacity and their tendency to decay over time (De Las Casas and Li, 2012). The performance of LIBs is dependent on the battery's electrochemical properties and these are mostly affected by the electrode materials. Electrode materials also determine the cost of preparing the LIBs (Lu *et al.*, 2021). The development of highly efficient electrodes is crucial for the next generation of lithium storage. The most commonly used anode material for LIBs is graphite. However, graphite has its shortcomings such as having a low reversible capacity and low diffusion rate which results in batteries with low power density. Hence there is a need for anode material improvement which may require the replacement of graphite anodes with materials with higher energy capacity, and power density coupled with good cycling life and safety risk-free. Given this, nano-sizing the anode materials could potentially improve these important properties, hence nanotubes from carbon present much promise and a bright perspective.

The unique properties of carbon nanotubes (CNTs) make them well suited as a critical component in novel anode material for enhanced lithium storage. Hence this study focuses on the improvement of the performance of LIBs through the application of CNTs as anode materials and optimisation of the electrochemical performance to create an ideal energy storage technology. The project is currently at TRL 3 and ongoing.

Titanium dioxide nanotubes for potassium-ion batteries

Currently, LIBs are being successfully used on a large scale for various applications, including in portable electronic devices as well as in automotive applications, due to their unique features such as high energy density and long life cycle. However, their feasibility and viability as a long-term solution is under question due to the scarcity and uneven geographical distribution of lithium resources (Zhang *et al.*, 2021). The scarcity of lithium is set to increase especially because of an expected increase in the demand for EVs. It is in this context that alternative energy storage systems become significant. Potassium-ion battery (KIB) is one of the latest entrants into this arena. Potassium-ion batteries are a potential alternative that utilise low cost and abundant potassium reserves on earth's crust. As nanomaterials are viable for energy storage, consequently, titanium dioxide nanomaterials are considered as a promising anode material for potassium/sodium/lithium-ion batteries due to their high safety, low cost, and moderate capacity. Therefore, titanium nanotubes were developed with enhanced properties that improve electrochemical characteristics to be used as anode for potassium-ion batteries using hydrothermal and anodisation methods. See Figure 1 for the working principle of potassium-ion batteries.

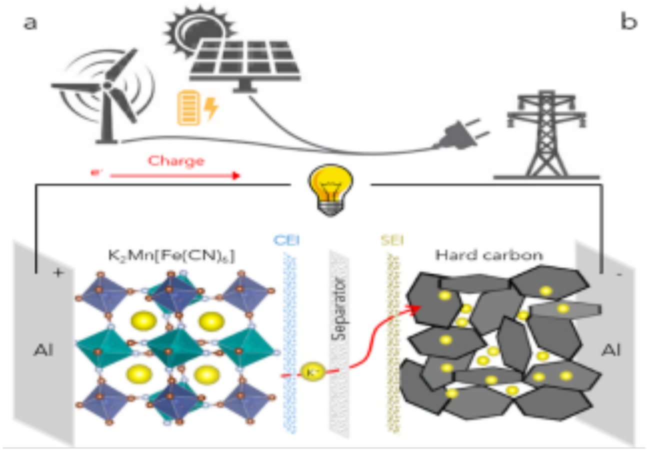


Figure 1. The working principle of potassium-ion batteries (Wu, 2021).

This project involves the synthesis of titanium dioxide nanotubes and other titanium dioxide based nanoparticles using both the hydrothermal and electrochemical anodisation methods. The in-depth characterisation of the materials is conducted using HRTEM, TEM, XRD amongst other techniques. Titanium dioxide nanomaterials are also be doped with various metals of interest in an attempt to achieve optimum characteristics required for energy storage materials. To test the activity of the materials, electrochemical characterisation and testing were conducted to establish materials' storage capacity and potential. To ensure that these materials can be commercialised, the project also involved lab-based scale-up studies from a few grams of the materials up to 100 grams, in preparation for future pilot studies, where kilograms will be manufactured. In this paper we demonstrate that titanium dioxide nanotubes have a superior ability to function as anode for potassium ion batteries compared to most materials used currently. Based on the results of our study, we intend comparing and contrasting the electrochemical activity of titanium dioxide nanotubes as anode materials for potassium ion batteries against currently used materials and advance the case for their large-scale application.

Techno economic study for recycling of lithium ion batteries in South Africa

The anticipated large number of spent LIBs joining the waste stream in the next decade is currently driving the global establishment of new recycling facilities. There is currently no LIB recycling facility in South Africa. A study was recently conducted by Mintek to determine if there is a business case for the establishment of a LIB recycling facility in South Africa. Although studies have previously been conducted on the LIB value chain, no study has been undertaken to assess the business case for establishing a LIB processing plant in South Africa. From a business perspective the information gained from the study is a critical first step that will inform decisions made on technology selection as well as the economic viability of the chosen technology, while from a policy perspective it is critical in determining the interventions required to unlock potential business opportunities in the LIB sector.

The objectives of this paper were three-fold:

- To provide an overview of the current state of the LIB recycling industry in South Africa.
- To assess commercial recycling technologies that are currently available and evaluate whether these technologies are suitable for local application.
- To conduct a techno-economic study to investigate the business case for the establishment of a LIB recycling plant in South Africa.

Currently China, Japan and South Korea collectively account for around 80% of global LIB production. A large proportion of international LIB recycling takes place near these LIB manufacturing facilities, since closed-loop systems with recycling at the end-of-life provide a source of recycled battery materials used by manufacturers for the production of new batteries. The anticipated large quantities of spent LIBs joining the waste stream from the EV sector are currently driving the establishment of new recycling facilities, especially in the northern hemisphere.

Very low volumes of waste LIB (between 6-10 tonnes per year), mainly from consumer electronics and ICT equipment, are currently collected locally. The estimated current installed LIB capacity in South Africa is around 5 000 tonnes, with around 1200 tonnes per annum available for recycling. The low volumes collected (estimated at around 1% of the available waste) are not sufficient to support a local recycling facility and as a result the current LIB waste in South Africa is either stockpiled, landfilled or shipped to recycling facilities around the globe.

Currently there are three recycling process options available for the processing of waste LIBs: pyrometallurgy, hydrometallurgy and direct recycling. Pyro- and hydrometallurgical technologies have been commercialised, whereas direct recycling is still in the research stage. These different processes can be combined in different flowsheet configurations, depending on factors such as quantity and characteristics of the material available and quantity and value of the materials that can be recovered. The hydrometallurgical route is favoured for new installations, specifically in China, the United States and Northern Europe.

Three generic flowsheets, pyrometallurgical, hydrometallurgical and physical processing to produce a black mass, were used to perform a techno-economic analysis. Based on the analysis, the most profitable recycling route is the production and sale of black mass, followed by the hydrometallurgical and pyrometallurgical routes. The analysis shows that recycling only becomes economical at a LIB feed rate of round 500 tonnes per annum for high-value batteries. For lower value batteries, the process becomes economical at much larger capacities. Profitability is very sensitive to the feed composition, specifically the Co, Ni and Cu content.

The conclusion from the study is that at the current low collection rates, there is not a business case for establishing a commercially viable LIB recycling plant in South Africa. The biggest driver for the establishment of such a facility would be the anticipated growth in the EV market. Recommendations following from the study include that:

- Strategies to increase the collection of LIBs be implemented.
- Government encourages the uptake of EVs in South Africa through acceleration of the implementation of South Africa's Green Transport Strategy; implementation of fiscal incentives to make EVs more cost-competitive and stimulate market penetration, and addressing issues related to the availability of charging stations, a reliable electricity supply and possibly setting manufacturing and sales targets as is being done elsewhere.
- Until such time as local volumes increase sufficiently to merit a local recycling facility, it is recommended that processes be implemented to treat LIBs to a stable state, after which it can be exported to international recycling facilities.
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Longer-term recommendations include:

- Installation of a small-scale mechanical plant for the pre-processing of the LIB waste to produce black mass, once collection rates around 500 tonnes per annum are reached. The black mass can be treated locally or exported to international refineries for metal recovery.
- A hydrometallurgical plant for the treatment of LIBs to produce either metal precipitates or high purity battery materials should be considered once the collection and availability of a reliable supply of large enough LIB waste volumes can be guaranteed (Gericke *et al*., 2021).

CONCLUSIONS

Mintek is strategically undertaking battery materials research across a number of disciplines including hydrometallurgy, pyrometallurgy and advanced materials. Both primary and secondary resources are explored as feed materials. The focus is on resource and energy efficiency as well as on the robustness of the flowsheets. In a region with a large extractive metallurgy industry, and given Mintek's position as a leading provider of minerals processing and metallurgical engineering products and services to industry, there is potential for Southern Africa to be a significant player in the battery materials value chain towards energy storage.

REFERENCES

Aguilar, M. and J.L. Cortina, Solvent extraction and liquid membranes: fundamentals and applications in new materials. 2008: CRC Press.

Ahmed, S., Nelson, P.A., Gallagher, K.G., Susarla, N. and Dees, D.W., Cost and energy demand of producing nickel manganese cobalt cathode material for lithium ion batteries. Journal of Power Sources, 2017. 342: p. 733-740.

Al-Thyabat, S., Nakamura, T., Shibala, E. and Lizuka, A., Adaptation of minerals processing operations for lithium-ion (LiBs) and nickel metal hydride (NiMH) batteries recycling: Critical review. Minerals Engineering, 2013. 45: p. 4-17.

Arancon, R.A.D., Lin, C.S.K., Chan, K.M., Kwan, T.H. and Luque, R., 2013. Advances on waste valorization: new horizons for a more sustainable society. Energy Science & Engineering, 1(2), pp.53-71.

Ballantyne A.D., Hallett J.P.,Riley D.J., Shah N. and Payne D.J., 2018. Lead acid battery recycling for the twenty-first century. Royal Society open science 5

Biswal, A., Tripathy, B.C., Subbaiah, T., Meyrick, D. and Minakshi, M., Electrodeposition of manganese dioxide: effect of quaternary amines. Journal of Solid State Electrochemistry, 2013. 17(5): p. 1349-1356.

Borah, R., Hughson, F.R., Johnston, J. and Nann, T., On battery materials and methods. Materials Today Advances, 2020. 6: p. 100046.

Bushveld Minerals, 2022. *Vanadium overview.* [Online] Available at: https://www.bushveldminerals.com/about-vanadium/
[Accessed 20 July 2022].

Coll, M., et al., Studies on the extraction of Co (II) and Ni (II) from aqueous chloride solutions using Primene JMT-Cyanex272 ionic liquid extractant. Hydrometallurgy, 2012. 125: p. 24-28.

Crundwell, F., Moats, M., Ramachandran, V., Robinson, T. and Davenport, W.G., Extractive metallurgy of nickel, cobalt and platinum group metals. 2011: Elsevier.

de Fátima da Silva, M., de Sousa Oliveira, M.R., dos Santos, I.D., Radino-Rouse, P. and Mansur, M.B., Iron precipitation strategies from nickel laterite ore sulfuric acid leach liquor. Mineral Processing and Extractive Metallurgy Review, 2022. 43(1): p. 28-39.

De Las Casas, C. and Li, W., "A review of application of carbon nanotubes for lithium ion battery anode material," J. Power Sources, vol. 208, pp. 74–85, 2012.

Department of Environment, Forestry and Fisheries (DEFF), 2020. National Waste Management Strategy,
https://www.dffe.gov.za/sites/default/files/docs/2020nationalwaste_managementstrategy1.pdf

Du Preez, A. and J. Preston, Separation of nickel and cobalt from calcium, magnesium and manganese by solvent extraction with synergistic mixtures of carboxylic acids. Journal of the Southern African Institute of Mining and Metallurgy, 2004. 104(6): p. 333-338.

Dutrizac, J., Factors affecting alkali jarosite precipitation. Metallurgical Transactions B, 1983. 14(4): p. 531-539.

Dzyazko, Y.S. and V.N. Belyakov, Purification of a diluted nickel solution containing nickel by a process combining ion exchange and electrodialysis. Desalination, 2004. 162: p. 179-189.

Gamali, I. and A. Vorozhko, CRYSTALLIZATION, STRUCTURE, AND HYDROGENATION OF ELECTROLYTIC MANGANESE. Sov. J. Electrochem.(English Translation edition), 1980. 16: p. 1011-1014.

Gao, F., Olayiwola, A.U., Liu, B., Wang, S., Du, H., Li, J., Wang, X., Chen, D. and Zhang, Y., 2022. Review of vanadium production part I: primary resources. Mineral Processing and Extractive Metallurgy Review, 43(4), pp.466-488.

Gericke, M., Nyanjowa, W. and Robertson, S., (2021) Technology landscape report and business case for the recycling of Li-ion batteries in South Africa. Available: https://wasteroadmap.co.za/wp-content/uploads/2021/05/30-Mintek-Final_Technical-report_LIB-plan.pdf (2022, July 18).

Goriparti, S., Miele, E., De Angelis, F., Di Fabrizio, E., Proietti Zaccaria, R. and Capiglia, C., "Review on recent progress of nanostructured anode materials for Li-ion batteries," J. Power Sources, vol. 257, pp. 421–443, 2014.

Goso, X., Lagendijk, H., Erwee, M. & Khosa, G., 2016. *Indicative Vanadium Deportment in the Processing of Titaniferous Magnetite by the Roast-Leach and Electric Furnace Smelting Processes.* Cape Town, The Southern African Institute of Mining and Metallurgy, pp. 69-80.

Harper, G., Sommerville, R., Kendrick, E., Driscoll, L., Slater, P., Stolkin, R., Walton, A., Christensen, P., Heidrich, O., Lambert, S. and Abbott, A., 2019. Recycling lithium-ion batteries from electric vehicles. Nature, 575(7781), pp.75-86.

Harris, M., Meyer, DM and K. Auerswald, The production of electrolytic manganese in South Africa. Journal of the Southern African Institute of Mining and Metallurgy, 1977. 77(7): p. 137-142.

Huang, B., Pan, Z., Su, X. and An, L., 2018. Recycling of lithium-ion batteries: Recent advances and perspectives. Journal of Power Sources, 399, pp.274-286.

Huang, Y., Zhang, Z., Cao, Y., Han, G., Peng, W., Zhu, X., Zhang, T.A. and Dou, Z., Overview of cobalt resources and comprehensive analysis of cobalt recovery from zinc plant purification residue- a review. Hydrometallurgy, 2020. 193: p. 105327.

Judge, W. and G. Azimi, Recent progress in impurity removal during rare earth element processing: A review. Hydrometallurgy, 2020. 196: p. 105435.

Karrech, A., Azadi, M.R., Elchalakani, M., Shahin, M.A. and Seibi, A.C., "A review on methods for liberating lithium from pegmatities," Miner. Eng., vol. 145, no. September 2019, p. 106085, 2020.

Lee, J.-c. Kurniwan, K., Kim, E.-y., Chung, K.W., Kim, R. and Jeon, H.-s., 2021. A review on the metallurgical recycling of vanadium from slags: towards a sustainable vanadium production. *Journal of Materials Research and Technology,* pp. 343-364.

Lekobotja, M., Mojapelo, M., Goso, X. C. & Lagendijk, H., 2017. *Recovery of vanadium from discard titaniferous magnetite.* Pretoria, Proceedings of the third Young Professionals Conference: The Southern African Institute of Mining and Metallurgy, pp. 351-354.

Lewis, A.E., Review of metal sulphide precipitation. Hydrometallurgy, 2010. 104(2): p. 222-234.

Li, M., Liu, J. and Han W. 2016. Recycling and management of waste lead-acid batteries: A mini-review.Waste Management and Research 34, 298–306.

Liu, B., Zhang, Y., Lu, M., Su, Z., Li, G. and Jiang, T., Extraction and separation of manganese and iron from ferruginous manganese ores: A review. Minerals Engineering, 2019. 131: p. 286-303.

Lu, J., D. Dreisinger, and T. Glück, Manganese electrodeposition—a literature review. Hydrometallurgy, 2014. 141: p. 105-116.

Lu, K., Zhao, C. and Jiang, Y., "Research progress of cathode materials for lithium-ion batteries," in E3S Web of Conferences, 2021, vol. 233.

Makuza, B., Tian, Q., Guo, X., Chattopadhyay, K. and Yu, D., 2021. Pyrometallurgical options for recycling spent lithium-ion batteries: A comprehensive review. Journal of Power Sources, 491, p.229-250.

Masiiwa, H., Mathe, O., Donegan, S., Nel, G., du Preez, R., Kotze, M. and Ireland, N., Evaluation of Versatic 10 and Versatic 10/Nicksyn™ synergistic systems for nickel-calcium separation on the Tati BMR hydrometallurgical demonstration plant. Proceedings of ISEC 2008, 2008: p. 169-175.

Mitchell, P. S., 2000. *The use of vanadium in steel.* Guilin, China, Proceedings of the Vanitec symposium.

Muller, P., "Is South Africa set to miss out on the global battery metals boom? https://m.miningweekly.com/article/is-south-africa-set-to-miss-out-on-...," no. August 2018, pp. 1–7, 2018, Accessed: Jan. 04, 2021. [Online]. Available: https://m.miningweekly.com/article/is-south-africa-set-to-miss-out-on-the-global-battery-metals-boom-2018-07-19.

Nasser, O.A. and M. Petranikova, Review of Achieved Purities after Li-ion Batteries Hydrometallurgical Treatment and Impurities Effects on the Cathode Performance. Batteries, 2021. 7(3).

Nkosi, S., Dire, P., Nyambeni, N. & Goso, X. C., 2017. *A comparative study of vanadium recovery from titaniferous magnetite using salt, sulphate, and soda ash roast-leach processes.* Pretoria, Proceedings of the third Young Professionals Conference: The Southern African Institute of Mining and Metallurgy.

Peek, E., T. Åkre, and E. Asselin, Technical and business considerations of cobalt hydrometallurgy. Jom, 2009. 61(10): p. 43-53.

Peng, F., Mu, D., Li, R., Liu, Y., Ji, Y., Dai, C. and Ding, F., Impurity removal with highly selective and efficient methods and the recycling of transition metals from spent lithium-ion batteries. RSC advances, 2019. 9(38): p. 21922-21930.

Roskill, 2010. *Vanadium: Global industry market and outlook, 12th Edition.* s.l.:Roskill information services Ltd.

Salakjani, N.K., Singh, P. and Nikoloski, A.N., "Production of Lithium –A Literature Review. Part 2. Extraction from Spodumene," Mineral Processing and Extractive Metallurgy Review. Taylor & Francis, 2019.

Sharma, I.G., Alex, P., Bidaye, A.C. and Suri, A.K., Electrowinning of cobalt from sulphate solutions. Hydrometallurgy, 2005. 80(1): p. 132-138.

Shen, X.y., Shao, H.M., Wang, J.D. and Zhai, Y.C., Preparation of ammonium jarosite from clinker digestion solution of nickel oxide ore roasted using (NH4)2SO4. Transactions of Nonferrous Metals Society of China, 2013. 23(11): p. 3434-3439.

Shvab, N., MANGANESE CORROSION IN SULFATE SOLUTION IN PRESENCE OF COBALT, NICKEL AND COPPER IONS. Ukrainskii Khimicheskii Zhurnal, 1972. 38(11): p. 1103-&.

Sole, K.C. and P.M. Cole, Purification of nickel by solvent extraction. Ion exchange and solvent extraction, 2001. 15: p. 143-195.

Steele, T. W. & Wilson, A., 1966. *A study of the salt-roast process for the extraction of vanadium from iron ore.* Brussels, Proceedings of the 36th Congress International De Chimie Industrielle, pp. 1-6.

Tawane, G., Maluleke, K., Goso, X. & Mokone, T., 2021. *Extraction of vanadium from discard titaniferous slag using sulfation roasting process.* s.l., Proceedings of the 7th International Slag Valorisation Symposium.

Vanadium Resources Limited, 2020. *Vanadium Resources Limited Announces the Results of Downstream Testwork on Samples from the Company's Steelpoortdrift Vanadium Project in South Africa.* [Online] Available at: https://www.marketscreener.com/quote/stock/VANADIUM-RESOURCES-LIMITE-65219224/news/Vanadium-Resources-Limited-Announces-the-Results-of-Downstream-Testwork-on-Samples-from-the-Company-33777025/ [Accessed 20 07 2022].

Wu, Z., Zou, J., Chen, S., Niu, X., Liu, J., Wang, L., "Potassium-ion battery cathodes: Past, present, and prospects", Journal of Power Sources, 484 (2021) 2290307

Yuan, R. Li, S., Che, Y., He, J., Song, J. and Yang, Bin., 2021. A critical review on extraction and refining of vanadium metal. *International Journal of Refractory Metals and Hard Materials,* Volume 101, pp. 1-12.

Yue, T., Han, H., Sun, W., Hu, Y., Chen, P. and Liu, R., Low-pH mediated goethite precipitation and nickel loss in nickel hydrometallurgy. Hydrometallurgy, 2016. 165: p. 238-243.

Zhang, J., Lai, L., Wang, H., Chen, M., Shen, Z.X., "Energy storage mechanisms of anode materials for potassium ion batteries". Materials Today Energy 21 (2021) 100747

Zhang, X., Tian, J., Hu, Y., Han, H., Luo, X., Sun, W., Yue, T., Wang, L., Cao, X. and Zhou, H., Selective sulfide precipitation of copper ions from arsenic wastewater using monoclinic pyrrhotite. Science of the Total Environment, 2020. 705: p. 135816.

Zosimovich, D., N. Shvab, and V. BELINSKY, Electrodeposition of manganese on a rotating electrode in the presence of impurities. ELEKTROKHIMIYA, 1967. 3(12): p. 1481-1485.

Buhle Sinaye Xakalashe

Mintek

Buhle has over 15 years of research and development experience in the field of extractive metallurgy from the following local and global institutions: Mintek (South Africa), NTNU/SINTEF (Norway), RWTH Aachen University (Germany), KU Leuven (Belgium) and the National Technical University of Athens (NTUA) (Greece). He has industrial experience through a stint at TRONOX Namakwa Sands' DC arc furnace operation for the production of high TiO_2 slag and pig iron. Buhle is currently the Head of New Technology in the Pyrometallurgy Division at Mintek. He is a member of the Technical Programme; Diversity and Inclusion in the Minerals Industry (DIMI); Environmental, Social, Governance and Sustainability (ESGS) committees of the Southern African Institute of Mining and Metallurgy (SAIMM). He contributes to organising of conferences including but not limited to the Furnace Tapping Conference 2014, Mine-Impacted Water Conferences (2020 & 2022), Southern African Rare Earths International Conference 2021 and the 8th International PGM Conference 2022. Buhle is passionate about batteries, particularly battery recycling towards a circular economy.