

# Metal recovery from spent lithium-ion batteries cathode materials: Comparative study of sugar-based reductants

Emenike G. Okonkwo<sup>a,b</sup>, Greg Wheatley<sup>a</sup>, Yang Liu<sup>a</sup>, Yinghe He<sup>a,c,\*</sup>

<sup>a</sup> College of Science and Engineering, James Cook University, Townsville, Australia

<sup>b</sup> Department of Metallurgical and Materials, University of Nigeria, Nsukka, Nigeria

<sup>c</sup> Department of Chemical Engineering, Brunel University London, Uxbridge, United Kingdom

## ARTICLE INFO

### Keywords:

Leaching  
Sugarcane molasses  
Sugar-based reductants  
Spent lithium-ion batteries  
Carbohydrates

## ABSTRACT

Sugars and sugar-rich agricultural by-products are cheaper and eco-friendly alternatives to conventional reductants used in recovering metals from spent lithium-ion batteries. Still, they are rarely used due to a poor understanding of their performance and reaction chemistry. In this study, two hypotheses bearing on the role of chemistry and influence of non-sugary organic compounds (impurities) on the performance of sugars, namely: glucose, fructose and sucrose, and a parent sugar-rich agro-industrial by-product – molasses, as reductants in the leaching of Li, Co, Mn and Ni from spent lithium-ion battery cathode material were tested. Statistical analysis using ANOVA revealed that the performance of the sugars and molasses are similar with >85% Mn, >88% Ni, >88%Co and >98% Li leached at 90 °C and 60 min. This shows that the presence of non-sugar organic compounds does not hamper the performance of the sugars-based reductants. The performance of the sugars relies more on temperature than chemistry. Furthermore, evaluation of the oxidation pathway hints at a potential inhibition of secondary oxidation reactions at lower temperatures. This study provides statistically validated proof that the performance of sugarcane molasses, even at lower concentration, is equipollent to the pure sugars in the leaching of critical metals from spent lithium-ion batteries.

## 1. Introduction

The deliberate transition to greener energy sources and high demand for lithium-ion battery powered devices, including electric vehicles is creating a surge in the demand for materials; notably battery metals such as cobalt, lithium, manganese and nickel (Chen et al., 2022). Battery metals are currently in high demand and are experiencing huge price fluctuations (Azevedo et al., 2018; Chen et al., 2022; IEA, 2022). Consequently, there is a growing interest in exploring strategies to sustain the supply and alleviate the price fluctuation of these metals; herein, recycling of spent batteries has been identified as a potential strategy (Mao et al., 2022; Zhang et al., 2015). Recycling is essential in this era of dwindling quantity of high-grade mineral ores, increasing quantity of spent batteries and need for proper disposal of waste batteries. This is because spent batteries are cheap and contain appreciable amount of battery metals (Okonkwo et al., 2021; Yang et al., 2021). Recycling can also help to mitigate the environmental impact of toxic components of spent batteries and the life cycle environmental impact of the batteries (Chen et al., 2022; Cheng et al., 2022; Okonkwo et al.,

2021).

The growing interest and need to recover metals from spent lithium-ion batteries is reflected by the increasing number of research articles, government policies and business start-ups in this area (Mao et al., 2022). The common methods employed to recover these metals include the pyro- and hydro-metallurgical based approaches synonymous to that for extracting these metals from their mineral (Raj et al., 2022; Yang et al., 2021). Hydrometallurgical approach is the most widely investigated and commercialized, and involves key steps such as leaching, in which reductants assist in the solubilization of the metals (Cheng et al., 2022; Okonkwo et al., 2021). Reductants (reducing agents) lowers the oxidation of transition metals (Co, Mn and Ni) present in spent batteries, making them amenable for dissolution by the lixiviant, hence are critical to the success of the hydrometallurgical based approach (Cheng et al., 2022; Ma et al., 2021; Meng et al., 2017)

Many reducing agents have been employed in the recovery of metals from spent batteries. Inorganic reductants such as H<sub>2</sub>O<sub>2</sub>, NaHSO<sub>3</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub>, hydrazine sulfate are quite common. Although very efficient, H<sub>2</sub>O<sub>2</sub> is thermally unstable whereas NaHSO<sub>3</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub>, hydrazine

\* Corresponding author at: Department of Chemical Engineering, Brunel University London, Uxbridge, United Kingdom.

E-mail address: [yinghe.he@brunel.ac.uk](mailto:yinghe.he@brunel.ac.uk) (Y. He).

<https://doi.org/10.1016/j.hazl.2024.100104>

Received 3 January 2024; Received in revised form 23 February 2024; Accepted 28 February 2024

Available online 1 March 2024

2666-9110/© 2024 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

sulfate are expensive, toxic and release toxic gases (e.g.  $\text{SO}_2$ ) (Chen et al., 2019; Meng et al., 2017). As an alternative, organic reductants such as carbohydrates (glucose, sucrose, cellulose, lactose), biomass (waste tea bag, grape seed, orange peels) and organic acids (ascorbic acid, formic acid and oxalic acid) were also utilized (Chen et al., 2018; Okonkwo et al., 2021; Refly et al., 2020). Organic reductants have the advantage of cost, availability and biodegradability/zero environmental impact (Okonkwo et al., 2021).

Carbohydrates especially glucose and sucrose has been extensively utilized in the recovery of transition metals (e.g., manganese) from mineral ores, spent zinc-alkaline cell batteries, etc. (Furlani et al., 2009, 2006; Wang et al., 2017). The performance of pure carbohydrates drew attention to the potential use of agro-industrial by-products such as molasses and whey, which are known to contain substantial quantity of these carbohydrates, are cheaper, more abundant and like spent batteries can also cause soil and water pollution (Su et al., 2009). It has been suggested that these sugar-rich agro-industrial by-products are cheaper alternatives for glucose and sucrose (Furlani et al., 2009; Golmohammadzadeh et al., 2017). Additionally, their application in the recovery of metals from spent lithium-ion batteries presents a zero-waste approach to manage both spent batteries and agro-industrial by-products. Presently, there are limited studies in this area, partly because of the fret over the potentially negative influence of non-sugary organic compounds (impurities), concern over annual output and poor understanding of reaction kinetics, pathway and mechanism (Sinha and Purcell, 2019).

Preliminary studies on the oxidation of these simple sugars using catalysts, ozone and metallic oxides show that carbohydrates undergoes hydrolysis, isomerization, dehydration, degradation reactions, with the products dependent on nature of media (acidic, neutral, alkaline), temperature and oxidant (Pagnanelli et al., 2014; Wojcieszak et al., 2017; Wrolstad, 2012; Zhang et al., 2021; Zhang and Huber, 2018). It is generally accepted that products including furfurals and lower molecular weight compounds such as gluconic acid, glucaric acid, formic acid and carbon dioxide, with reductive abilities are formed when carbohydrates are oxidized in acidic media (Baral et al., 2015; Lee et al., 2016; Pagnanelli et al., 2014). Except for glucose, there is limited experimental data on the performance and possible reaction pathway of the sucrose and fructose as reducing agent in the recovery of metals.

As a step to fill these gaps in the use of sugars and by-products of sugar production (sugarcane molasses) in the recovery of metals from spent lithium-ion batteries, this work compared the performance of different carbohydrates namely: glucose, sucrose, and fructose with each other and with sugarcane molasses, as reductants in the leaching of  $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$  cathode materials. The main objective is to evaluate the performance of the different sugars and by-product of sugar production as reducing agent and establish if the presence of non-sugary organic compounds as impurities in sugar-by products such as molasses hampers the leaching of cobalt, nickel, manganese and lithium from the cathode materials of spent lithium-ion batteries. To achieve this objective, we tested the following hypotheses: (1) Given their chemistry, the performance of glucose, fructose and sucrose will not be significantly different from each other. (2) The performance of molasses, due to the presence of other organic components as impurities in it, would be better or equivalent to those of the pure carbohydrates. Finally, a reaction pathway was provided.

## 2. Materials and method

### 2.1. Materials

Cathode materials were obtained from dismantled and pre-treated spent lithium-ion batteries, which were gathered from a local battery shop in Townsville. These cathode materials were homogenized by grinding in a ball mill and mixing using a mortar and pestle followed by sieving. The elemental composition of the cathode material obtained

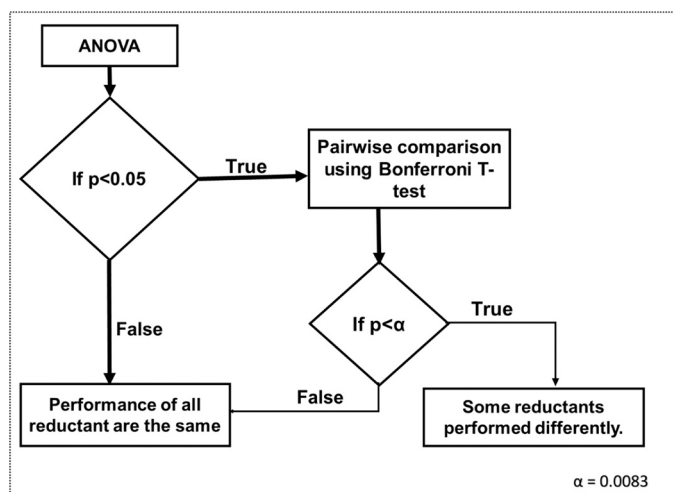


Fig. 1. Flowchart for statistical analysis.

through wet chemical analysis (aqua regia digestion,  $\text{HCl}:\text{HNO}_3$  3:1 v/v) is 6.2% Li, 13.2% Co, 19.0% Mn and 31.8% Ni. XRD analysis showing the phases present in the cathode material is shown in Fig. S1.

Sugarcane molasses was obtained from Wilmar Sugar mill. The sugar profile analysis is shown in Table S1 and Figure S2. Other chemicals used are D-Glucose (AR Grade, Ajax Finechem), D-fructose (>99%, Sigma Aldrich), sucrose (AR grade, Chem Supply), methanesulfonic acid (>99%, Sigma Aldrich).

### 2.2. Method

All leaching experiment were performed in a 250 mL glass reactor that was heated using a hot plate equipped with a magnetic stirring system. In each leaching test, 2.5 g of cathode material along with fixed amount of reductant were added to 50 mL of 2 M methanesulfonic acid solution that was already heated to the desired temperature. After leaching, the liquor were filtered using a vacuum filtration unit, and the residue dried for further analyses whereas a known volume of the filtrate is further diluted for quantification of the concentration of the metals. The dosage of reductant kept was kept at 0.4 g/g based on previous experiment backed by stoichiometric calculation (see equations S1 and S2), which shows the balanced reaction equation assuming an  $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$  (NCM 523) cathode material (Okonkwo et al., 2023). An agitation rate of 400 rpm was used in all the leaching test whereas leaching time and temperature were varied from 30 to 60 mins and 60–90 °C.

### 2.3. Analytical methods

Two basic analyses namely: chemical and statistical analyses were carried out to evaluate the performance of the sugars and sugarcane molasses and test our hypotheses.

Chemical analysis. The concentration of cobalt, manganese, nickel and lithium in the filtrate were quantified using inductively coupled plasma atomic emission spectroscopy (ICP-OES, Agilent Technologies). The obtained result were inputted in Eq. 3 to calculate the leaching efficiency of the metals.

$$\text{Leaching efficiency } (\%) = \frac{C_{i,l}}{C_{i,o}} \times 100 \quad (3)$$

Where  $C_{i,l}$  and  $C_{i,o}$  are the concentration of metal  $i$  in mg/g in the leach liquor and the cathode material, respectively.

The concentration of metal ( $C_i$ ) is given by the relation in Eq. (4)

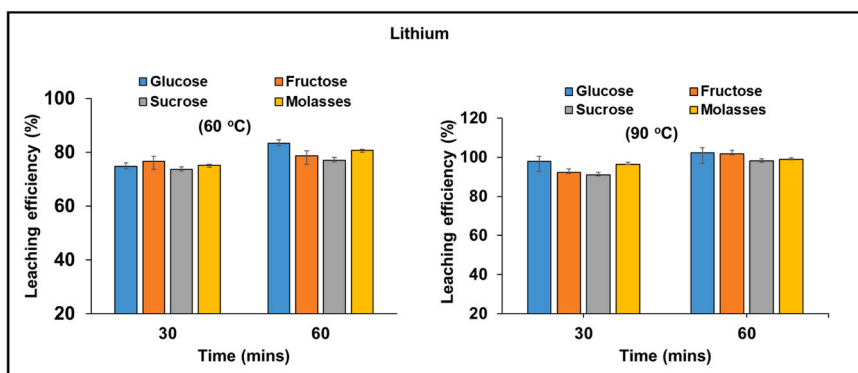


Fig. 2. Effect of sugar type on the leaching of lithium at different temperatures and times.

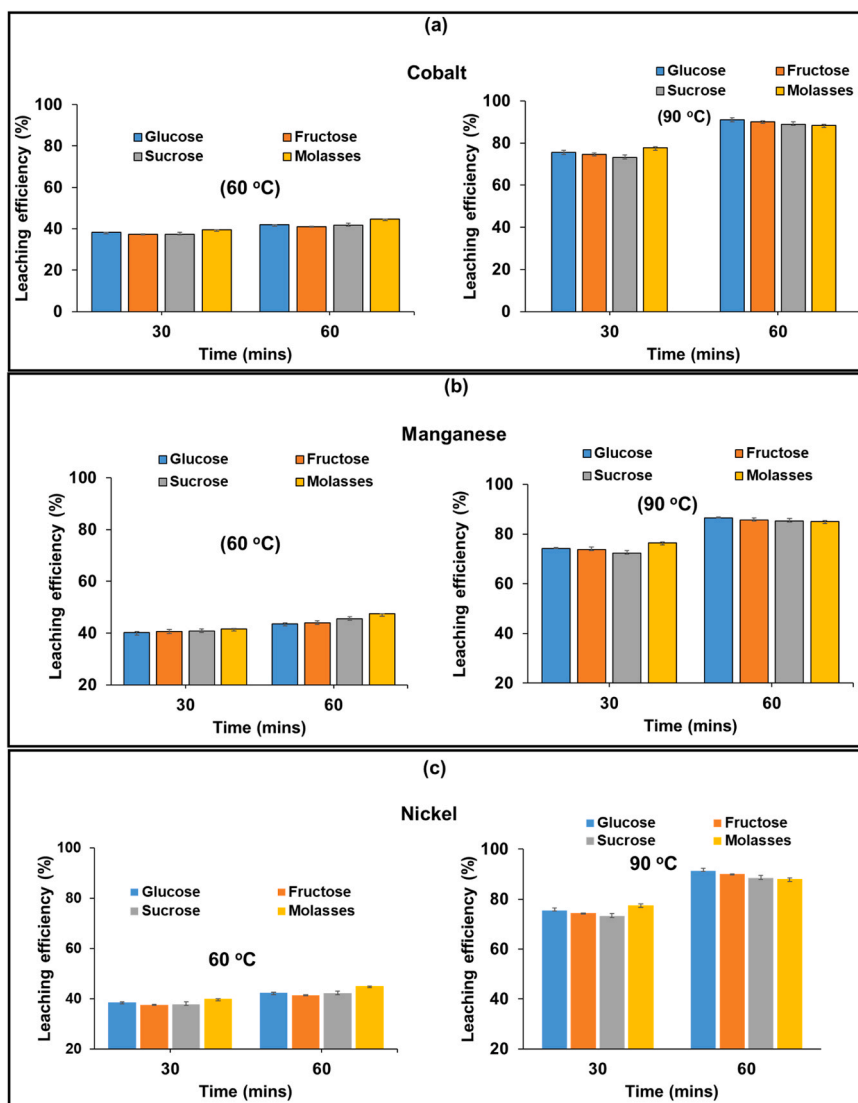


Fig. 3. Performance of sugars as reductants on the leaching of (a) cobalt (b)Manganese and (c) Nickel at different temperatures and times.

$$C_i(mg.g^{-1}) = \frac{c(mgL^{-1}) \times V(L)}{m(g)} \quad (4)$$

Where  $C_i$  is the concentration of metal i,  $c(mgL^{-1})$  is metal concentration obtained from ICP-AES analysis,  $V(L)$  is the volume of leaching solution,  $m(g)$  is the mass of cathode material used during digestion or leaching.

Statistical analysis. Significant differences between the leaching performance of the sugars and molasses were evaluated using analysis of variance (ANOVA) and Bonferroni T-test. The flowchart for statistical analysis is shown in Fig. 1. All statistical analysis were performed using Microsoft Excel 2016.

### 3. Result and discussion

#### 3.1. Influence of sugar type on the leaching of lithium

The leaching of lithium is neither affected by the sugar type nor the use of sugarcane molasses (Fig. 2). Statistically similar leaching efficiencies (see Table S2) were achieved by all the reductants. Whilst the presence of reducing agents aids the breakdown of the cathode material, and consequently the release of lithium; the leaching of lithium is an exchange reaction between  $\text{Li}^+$  in the cathode material and  $\text{H}^+$  from the acid, thus strongly dependent on the availability of protons ( $\text{H}^+$ ) (Billy et al., 2018; Gao et al., 2018; Xuan et al., 2019). This is because lithium is an alkali metal with an oxidation state of +1 in the cathode material hence does not require prior reduction (charge compensation) to be leached (Cheng et al., 2022).

Furthermore, the leaching of lithium shown in Fig. 2 is fast and strongly dependent on temperature. At 90 °C, above 90% of lithium can be leached in 30 min compared to >73% at 60 °C. Among all the metals present in the cathode material, lithium has the smallest ionic radius and weakest metal-oxygen bond, hence is easily leached out at a considerable temperature (Li et al., 2022). Comparatively, the observed influence of the different sugars and molasses on the leaching of lithium indicates that the non-sugary components of molasses were not inhibitory to the leaching reactions and might have facilitated it. Enhancement in leaching efficiency of lithium due to presence of non-sugary components has also been reported elsewhere (Chen et al., 2019; Wu et al., 2020; Zhang et al., 2018).

#### 3.2. Influence of sugar type on the leaching of the transition metals

Fig. 3 shows the influence of sugar type with respect to leaching temperature and time on the leaching of cobalt, manganese and nickel. It is evident that under a given temperature and time, the rate of sugar-like reactions such as hydrolysis, and the subsequent reduction of the transition metals by the reductants are comparable.

Regardless of the sugar type, the leaching of the transition metals improved with temperature, which is not surprising because of the endothermic nature of leaching processes (Meng et al., 2020). Statistically similar performance was achieved at elevated temperature (90 °C) and extended leaching time (60 mins) (see ANOVA result in Table S2) as well as at shorter leaching duration (see ANOVA result in Table S2 and Post Hoc Test in Table S3). However, and irrespective of leaching time, the performance of the reductants differed at lower temperature (60 °C). For instance, pairwise comparison of the leaching of cobalt and nickel at 60 °C after 60 mins showed that glucose and fructose exhibited leaching efficiencies that are significantly different from that of molasses but not from sucrose. It is noteworthy that although the observed leaching efficiencies of Co and Ni at 60 °C, 60 mins shown in Fig. 3a and 3b are statistically significant, the numerical difference are slight, hence negligible from the practical viewpoint. On the other hand, the performance of sucrose and molasses showed no notable difference. Oxidation of sugars by metals and metallic oxides is a multi-step chain-like reaction that involves several intermediate products, therefore, decreasing temperature might have hindered the ancillary oxidation processes (Jin et al., 2016; Miedziak et al., 2014; Qi et al., 2015). There is no explanation for this except that the rate of oxidation of secondary products such as gluconic acid is known to be slower than that of glucose to gluconic acid (Lee et al., 2016).

Time, especially at the lower temperature (60 °C) (see Fig. 3) played an insignificant role on the leaching of the transition metals. Irrespective of the reductant, less than 5% improvement in leaching efficiency were achieved at 60 °C by extending the leaching time from 30 mins to 60 mins. This shows that sugar hydrolysis is fast and the reduction of transition metals by carbohydrates is more temperature dependent than other subsequent possible reactions.

#### 3.3. Possible reaction chemistry and pathway of the sugars and molasses as reductants

The above leaching results show that in most cases, the sugars exhibited similar reductive abilities in the leaching of cobalt, manganese, nickel, and lithium from spent  $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$  cathode materials, which suggests similar oxidation mechanism. All reductants performed equally at high temperature (90 °C) irrespective of the duration of the leaching while statistically significant difference in performance between glucose/fructose and molasses were only recorded at low temperature and longer leaching time (60 °C, 60 mins). Sucrose demonstrated reductive ability significantly similar to molasses as well as both glucose and fructose. The observed performance of the sugars under different leaching conditions can be linked to their structure, reactivity, and reaction chemistry. A possible oxidation chemistry of the sugars and inherently during the reductive leaching process is presented in Figs. S3 and 4.

Chromatographic examination of the leachate after the precipitation of the leached metals and pH adjustment revealed the presence of organic compounds which are oxidation products of the sugars (Figure S4). However, further characterization of the formed oxidation products using standard chromatographic and spectrometric methods proved to be difficult because of the complex nature of the formed intermediate organic compounds. Therefore, inferences from peer reviewed articles were used to elucidate the oxidation mechanism for the sugars and inherently molasses.

Monosaccharides such as glucose and fructose, in mildly acidic and presence of an oxidant are known to undergo a series of reactions that yield shorter chained compounds (Derrien et al., 2017; Körner et al., 2019; Lee et al., 2016; Shallenberger and Mattick, 1983). Tentatively, glucose in its open chained structure is oxidized to gluconic acid via the oxidation of the aldehyde group (C1 carbon) or glucuronic acid via oxidation of the primary hydroxyl group (C6 carbon) (Cheng et al., 2019; Wrolstad, 2012). C-C cleavage to form formic acid has also been reported (Yin et al., 2020), but gluconic acid pathway is more thermodynamic favorable due to the high reducibility of the aldehyde group. Therefore, the oxidation to gluconic acid is bound to be the predominant pathway. Further oxidation of gluconic acid gives glucaric acid (Jin et al., 2016). The oxidation of gluconic acid to glucaric acid is facilitated by strong oxidizing environment such as that created by the spent cathode material, oxygen or hydrogen peroxide and rapid at high temperature (Lee et al., 2016; Zhuge et al., 2019). This implies that glucaric acid will dominate as the leaching reaction progresses especially at the higher leaching temperature, and might explain the trend observed by Pagnanelli et al., where the pathway of glucose oxidation during the leaching of lithium and cobalt from  $\text{LiCoO}_2$  cathode materials was found to be dependent on time of addition of the reductant. The authors noted that delayed addition of glucose during the leaching process (after 2hrs) favors the formation of glucaric acid due to the presence of more reactive Co(III) particles (higher specific surface area) (Pagnanelli et al., 2014). Secondary oxidation, fragmentation and redol-aldol reaction involving glucaric acid will lead to the formation of glyceric acid, tartaric acid, oxalic acid, formic acid, 2-keto gluconic acid and 5-keto gluconic acid among others as shown in Fig. S3 and previously reported (Lee et al., 2016; Zhang et al., 2021).

Fructose, although a ketone, is more reactive than glucose and known to take an open chained structure in aqueous solution (Eggleston and Vercellotti, 2000; Shallenberger and Mattick, 1983). The pathway of fructose oxidation in acidic media is poorly understood; however, isomerization to glucose and dehydration to hydroxymethylfurfural (HMF) and levulinic acid has been reported. Isomerization to glucose is favored by basic environment (Qi et al., 2015); therefore, fructose oxidation by the cathode materials utilized in this study might have proceeded via acid induced dehydration to HMF and subsequent oxidation of hydrated products to levulinic acid and formic acid and oxidation to carboxylic acids and furans (Körner et al., 2019; Wrolstad,

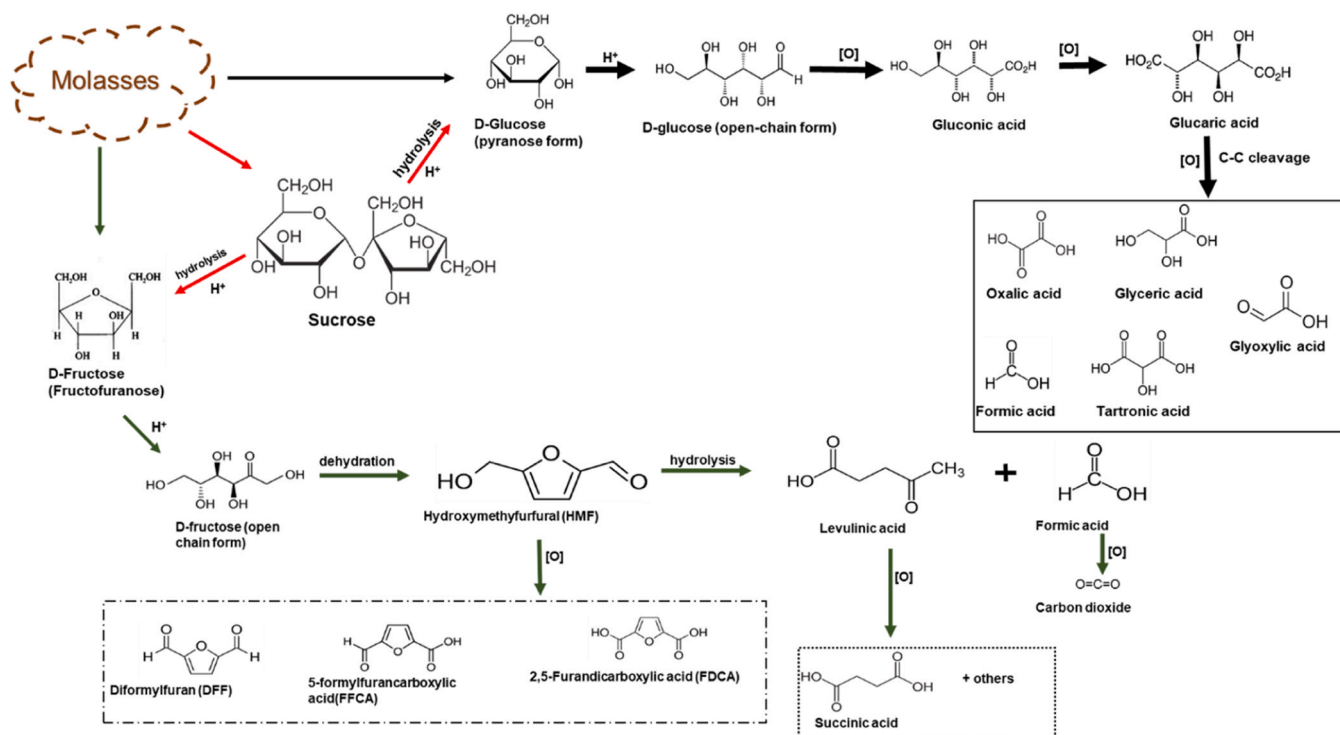


Fig. 4. Pathway of molasses oxidation during the reductive leaching of metals from LIB cathode material.

2012)

Unlike the monosaccharides, sucrose is hydrolyzed to glucose and fructose in acidic media (Wrolstad, 2012). A preliminary analysis of the plausible oxidation products of sucrose during the leaching of manganese from pyrolusite by Baral et al. revealed the presence of gluconic acid, glucaric acid and HMF (Baral et al., 2015), which are common oxidation products of glucose and fructose. Thus, it is plausible that sucrose degradation pathway is an amalgam of that of its principal components – glucose and fructose. Further confirmatory studies that would investigate the influence of cation type on the oxidation pathway are needed as they have been found to influence the formed oxidation product (Zhang et al., 2021).

With hindsight, the oxidation pathway of molasses can be inferred from those of its component sugars. Thus, the hydrolysis of sucrose to glucose and fructose and conversion of the inherent glucose and fructose to gluconic acid, HMF, levulinic acid humins etc. would occur concurrently, which would be accompanied by further oxidation to lower molecular weight compounds (see Fig. 4).

#### 4. Conclusion

A comparative analysis of the performance of different sugars and sugarcane molasses as reductants in the recovery of critical metals from spent lithium-ion batteries has been accomplished, and a tentative oxidation pathway drawn. Temperature played a significant role on the performance of all the reductants. The monosaccharides are representative of sucrose and molasses only at high temperature whereas is a statistically significant difference in their performance at low temperature. Low temperature might have hampered the rate of secondary oxidation reactions.

Statistical analysis using ANOVA ( $p = 0.05$ ) showed that there is negligible difference in the performance of the sugars. The observed similarity in the performance of the monosaccharides and sucrose shows that hydrolysis of sucrose is fast and not a rate limiting step. Similarly, non-sugar organic compounds (impurities) present in molasses did not hamper its reductive ability; in fact, they might have aided its

performance especially at lower temperature.

Overall, this study experimentally and statistically validates the claim that molasses is a cheaper substitute to glucose, sucrose and fructose. While this hints at a potentially similar oxidation pathway amongst the sugars and molasses as already highlighted, experimental validation is need; this will be the focus of our future study.

#### Funding information

There is no funding information to declare.

#### CRediT authorship contribution statement

**Emenike Okonkwo:** Writing – review & editing, Writing – original draft, Visualization, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Yang Liu:** Writing – review & editing, Visualization, Validation, Supervision, Methodology. **Greg Wheatley:** Visualization, Supervision, Software, Project administration. **Yinghe He:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.hazl.2024.100104](https://doi.org/10.1016/j.hazl.2024.100104).

## References

- Azevedo, M., Campagnoli, N., Hagenbruch, T., Hoffman, K., Lala, A., Ramsbottom, O., 2018. Lithium and cobalt - a tale of two commodities. *McKinsey&Company Metals and Mining*.
- Baral, A.B., Dash, B., Ghosh, M.K., Subbaiah, T., Minakshi, M., 2015. Pathway of sucrose oxidation in manganese (Pyrolusite) nodules. *Ind. Eng. Chem. Res.* 54, 12233–12241. <https://doi.org/10.1021/acs.iecr.5b02881>.
- Billy, E., Joulié, M., Laucourmet, R., Boulineau, A., De Vito, E., Meyer, D., 2018. Dissolution mechanisms of LiNi<sub>1</sub>/3Mn<sub>1</sub>/3Co<sub>1</sub>/3O<sub>2</sub> positive electrode material from lithium-ion batteries in acid solution. *ACS Appl. Mater. Interfaces* 10, 16424–16435. <https://doi.org/10.1021/acsami.8b01352>.
- Chen, H., Hu, P., Wang, D., Liu, Z., 2022. Selective leaching of Li from spent LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> cathode material by sulfation roast with NaHSO<sub>4</sub>H<sub>2</sub>O and water leach. *Hydrometallurgy* 210, 105865. <https://doi.org/10.1016/j.hydromet.2022.105865>.
- Chen, X., Guo, C., Ma, H., Li, J., Zhou, T., Cao, L., Kang, D., 2018. Organic reductants based leaching: a sustainable process for the recovery of valuable metals from spent lithium ion batteries. *Waste Manag* 75, 459–468. <https://doi.org/10.1016/j.wasman.2018.01.021>.
- Chen, Y., Chang, D., Liu, N., Hu, F., Peng, C., Zhou, X., He, J., Jie, Y., Wang, H., Wilson, B.P., Lundstrom, M., 2019. Biomass-assisted reductive leaching in H<sub>2</sub>SO<sub>4</sub> medium for the recovery of valuable metals from spent mixed-type lithium-ion batteries. *Jom* 71, 4465–4472. <https://doi.org/10.1007/s11837-019-03775-3>.
- Cheng, M., Zhang, Q., Yang, C., Zhang, B., Deng, K., 2019. Photocatalytic oxidation of glucose in water to value-added chemicals by zinc oxide-supported cobalt thiophosphazine. *Catal. Sci. Technol.* 9, 6909–6919. <https://doi.org/10.1039/c9cy01756a>.
- Cheng, X., Guo, C., Cheng, Y., Liu, M., Ji, J., 2022. Effect of hydrogen peroxide on the recovery of valuable metals from spent LiNi<sub>0.6</sub>Co<sub>0.2</sub>Mn<sub>0.2</sub>O<sub>2</sub> batteries. *Energy Technol.* 10, 1–12. <https://doi.org/10.1002/ente.202200039>.
- Derrien, E., Mounguengui-Diallo, M., Perret, N., Marion, P., Pinel, C., Besson, M., 2017. Aerobic oxidation of glucose to gluconic acid under alkaline-free conditions: au-based bimetallic catalysts and the effect of residues in a hemicellulose hydrolysate. *Ind. Eng. Chem. Res.* 56, 13175–13189. <https://doi.org/10.1021/acs.iecr.7b01571>.
- Eggleston, G., Vercellotti, J.R., 2000. Degradation of sucrose, glucose and fructose in concentrated aqueous solutions under constant pH conditions at elevated temperature. *J. Carbohydr. Chem.* 19, 1305–1318. <https://doi.org/10.1080/07328300008544153>.
- Furlani, G., Moscardini, E., Pagnanelli, F., Ferella, F., Vegliò, F., Toro, L., 2009. Recovery of manganese from zinc alkaline batteries by reductive acid leaching using carbohydrates as reductant. *Hydrometallurgy* 99, 115–118. <https://doi.org/10.1016/j.hydromet.2009.07.005>.
- Furlani, G., Pagnanelli, F., Toro, L., 2006. Reductive acid leaching of manganese dioxide with glucose: identification of oxidation derivatives of glucose. *Hydrometallurgy* 81, 234–240. <https://doi.org/10.1016/j.hydromet.2005.12.008>.
- Gao, W., Liu, C., Cao, H., Zheng, X., Lin, X., Wang, H., Zhang, Y., Sun, Z., 2018. Comprehensive evaluation on effective leaching of critical metals from spent lithium-ion batteries. *Waste Manag.* 75, 477–485. <https://doi.org/10.1016/j.wasman.2018.02.023>.
- Golmohammadzadeh, R., Rashchi, F., Vahidi, E., 2017. Recovery of lithium and cobalt from spent lithium-ion batteries using organic acids: Process optimization and kinetic aspects. *Waste Manag.* 64, 244–254. <https://doi.org/10.1016/j.wasman.2017.03.037>.
- IEA, 2022. Critical minerals threaten a decades-long trend of cost declines for clean energy technologies. IEA.
- Jin, X., Zhao, M., Vora, M., Shen, J., Zeng, C., Yan, W., Thapa, P.S., Subramaniam, B., Chaudhari, R.V., 2016. Synergistic effects of bimetallic PtPd/TiO<sub>2</sub> nanocatalysts in oxidation of glucose to gluconic acid: structure dependent activity and selectivity. *Ind. Eng. Chem. Res.* 55, 2932–2945. <https://doi.org/10.1021/acs.iecr.5b04841>.
- Körner, P., Jung, D., Kruse, A., 2019. Influence of the pH value on the hydrothermal degradation of fructose. *ChemistryOpen* 8, 1121–1132. <https://doi.org/10.1002/open.201900225>.
- Lee, J., Saha, B., Vlachos, D.G., 2016. Pt catalysts for efficient aerobic oxidation of glucose to gluconic acid in water. *Green. Chem.* 18, 3815–3822. <https://doi.org/10.1039/c6gc00460a>.
- Li, P., Luo, S.H., Su, F., Zhang, L., Yan, S., Lei, X., Mu, W., Wang, Q., Zhang, Y., Liu, X., Hou, P., 2022. Optimization of synergistic leaching of valuable metals from spent lithium-ion batteries by the sulfuric acid-malonic acid system using response surface methodology. *ACS Appl. Mater. Interfaces* 14, 11359–11374. <https://doi.org/10.1021/acsami.1c23258>.
- Ma, Y., Zhou, X., Tang, J., Liu, X., Gan, H., Yang, J., 2021. Reaction mechanism of antibiotic bacteria residues as a green reductant for highly efficient recycling of spent lithium-ion batteries. *J. Hazard. Mater.* 417, 126032 <https://doi.org/10.1016/j.jhazmat.2021.126032>.
- Mao, J., Ye, C., Zhang, S., Xie, F., Zeng, R., Davey, K., Guo, Z., Qiao, S., 2022. Toward practical lithium-ion battery recycling: adding value, tackling circularity and recycling-oriented design. *Energy Environ. Sci.* <https://doi.org/10.1039/d2ee00162d>.
- Meng, F., Liu, Q., Kim, R., Wang, J., Liu, G., Ghahreman, A., 2020. Selective recovery of valuable metals from industrial waste lithium-ion batteries using citric acid under reductive conditions: leaching optimization and kinetic analysis. *Hydrometallurgy* 191, 1–11. <https://doi.org/10.1016/j.hydromet.2019.105160>.
- Meng, Q., Zhang, Y., Dong, P., 2017. Use of glucose as reductant to recover Co from spent lithium ions batteries. *Waste Manag.* 64, 214–218. <https://doi.org/10.1016/j.wasman.2017.03.017>.
- Miedzziak, P.J., Alshammari, H., Kondrat, S.A., Clarke, T.J., Davies, T.E., Morad, M., Morgan, D.J., Willock, D.J., Knight, D.W., Taylor, S.H., Hutchings, G.J., 2014. Base-free glucose oxidation using air with supported gold catalysts. *Green. Chem.* 16, 3132–3141. <https://doi.org/10.1039/c4gc00087k>.
- Okonkwo, E.G., Wheatley, G., He, Y., 2021. The role of organic compounds in the recovery of valuable metals from primary and secondary sources: a mini-review. *Resour. Conserv. Recycl.* 174, 105813 <https://doi.org/10.1016/j.resconrec.2021.105813>.
- Okonkwo, E.G., Wheatley, G., Liu, Y., He, Y., 2023. Green and efficient recovery of valuable metals from spent lithium-ion batteries using molasses: parametric optimization and performance evaluation. *Hydrometallurgy* 222, 106168. <https://doi.org/10.1016/j.hydromet.2023.106168>.
- Pagnanelli, F., Moscardini, E., Granata, G., Cerbelli, S., Agosta, L., Fieramosca, A., Toro, L., 2014. Acid reducing leaching of cathodic powder from spent lithium ion batteries: glucose oxidative pathways and particle area evolution. *J. Ind. Eng. Chem.* 20, 3201–3207. <https://doi.org/10.1016/j.jiec.2013.11.066>.
- Qi, P., Chen, S., Chen, J., Zheng, J., Zheng, X., Yuan, Y., 2015. Catalysis and reactivation of ordered mesoporous carbon-supported gold nanoparticles for the base-free oxidation of glucose to gluconic acid. *ACS Catal.* 5, 2659–2670. <https://doi.org/10.1021/cs502093b>.
- Raj, T., Chandrasekar, K., Kumar, A.N., Sharma, P., Pandey, A., Jang, M., Jeon, B.H., Varjani, S., Kim, S.H., 2022. Recycling of cathode material from spent lithium-ion batteries: challenges and future perspectives. *J. Hazard. Mater.* 429, 128312 <https://doi.org/10.1016/j.jhazmat.2022.128312>.
- Refly, S., Floweri, O., Mayangsari, T.R., Aimon, A.H., Iskandar, F., 2020. Green recycle processing of cathode active material from LiNi<sub>1</sub>/3Co<sub>1</sub>/3Mn<sub>1</sub>/3O<sub>2</sub>(NCM 111) battery waste through citric acid leaching and oxalate co-precipitation process. *Mater. Today Proc.* 44, 3378–3380. <https://doi.org/10.1016/j.matpr.2020.11.664>.
- Shallenberger, R.S., Mattick, L.R., 1983. Relative stability of glucose and fructose at different acid pH. *Food Chem.* 12, 159–165. [https://doi.org/10.1016/0308-8146\(83\)90002-X](https://doi.org/10.1016/0308-8146(83)90002-X).
- Sinha, M.K., Purcell, W., 2019. Reducing agents in the leaching of manganese ores: a comprehensive review. *Hydrometallurgy* 187, 168–186. <https://doi.org/10.1016/j.hydromet.2019.05.021>.
- Su, H., Wen, Y., Wang, F., Li, X., Tong, Z., 2009. Leaching of pyrolusite using molasses alcohol wastewater as a reductant. *Miner. Eng.* 22, 207–209. <https://doi.org/10.1016/j.mineng.2008.05.006>.
- Wang, Y., Jin, S., Lv, Y., Zhang, Y., Su, H., 2017. Hydrometallurgical process and kinetics of leaching manganese from semi-oxidized manganese ores with sucrose. *Minerals* 7, 1–13. <https://doi.org/10.3390/min7020027>.
- Wojcieszak, R., Ferraz, C.P., Sha, J., Houda, S., Rossi, L.M., Paul, S., 2017. Advances in base-free oxidation of bio-based compounds on supported gold catalysts. *Catalysts* 7, 1–23. <https://doi.org/10.3390/catal7110352>.
- Wroldstad, R.E., 2012. *Food carbohydrate chemistry*, 1st ed. John Wiley & Sons.
- Wu, Z., Soh, T., Chan, J.J., Meng, S., Meyer, D., Srinivasan, M., Tay, C.Y., 2020. Repurposing of fruit peel waste as a green reductant for recycling of spent lithium-ion batteries. *Environ. Sci. Technol.* 54, 9681–9692. <https://doi.org/10.1021/acs.est.0c02873>.
- Xuan, W., Otsuki, A., Chagnes, A., 2019. Investigation of the leaching mechanism of NMC 811 (LiNi<sub>0.8</sub>Mn<sub>0.1</sub>Co<sub>0.1</sub>O<sub>2</sub>) by hydrochloric acid for recycling lithium ion battery cathodes. *RSC Adv.* 9, 38612–38618. <https://doi.org/10.1039/c9ra06686a>.
- Yang, Y., Okonkwo, E.G., Huang, G., Xu, S., Sun, W., He, Y., 2021. On the sustainability of lithium ion battery industry – a review and perspective. *Energy Storage Mater.* 36, 186–212. <https://doi.org/10.1016/j.ensm.2020.12.019>.
- Yin, J., Zhang, Q., Yang, C., Zhang, B., Deng, K., 2020. Highly selective oxidation of glucose to gluconic acid and gluconic acid in water catalyzed by an efficient synergistic photocatalytic system. *Catal. Sci. Technol.* 10, 2231–2241. <https://doi.org/10.1039/c9cy02393c>.
- Zhang, Q., Wan, Z., Yu, I.K.M., Tsang, D.C.W., 2021. Sustainable production of high-value gluconic acid and gluconic acid through oxidation of biomass-derived glucose: a critical review. *J. Clean. Prod.* 312, 127745 <https://doi.org/10.1016/j.jclepro.2021.127745>.
- Zhang, X., Cao, H., Xie, Y., Ning, P., An, H., You, H., Nawaz, F., 2015. A closed-loop process for recycling LiNi<sub>1</sub>/3Co<sub>1</sub>/3Mn<sub>1</sub>/3O<sub>2</sub> from the cathode scraps of lithium-ion batteries: process optimization and kinetics analysis. *Sep. Purif. Technol.* 150, 186–195. <https://doi.org/10.1016/j.seppur.2015.07.003>.
- Zhang, Y., Meng, Q., Dong, P., Duan, J., Lin, Y., 2018. Use of grape seed as reductant for leaching of cobalt from spent lithium-ion batteries. *J. Ind. Eng. Chem.* 66, 86–93. <https://doi.org/10.1016/j.jiec.2018.05.004>.
- Zhang, Z., Huber, G.W., 2018. Catalytic oxidation of carbohydrates into organic acids and furan chemicals. *Chem. Soc. Rev.* 47, 1351–1390. <https://doi.org/10.1039/c7cs00213k>.
- Zhuge, Y., Fan, G., Lin, Y., Yang, L., Li, F., 2019. A hybrid composite of hydroxyapatite and Ca-Al layered double hydroxide supported Au nanoparticles for highly efficient base-free aerobic oxidation of glucose. *Dalton Trans.* 48, 9161–9172. <https://doi.org/10.1039/c9dt00985j>.