SSRG International Journal of Recent Engineering Science
ISSN: 2349–7157 / https://doi.org/10.14445/23497157/IJRES-V11I5P104

Volume 11 Issue 5, 33-39, Sep-Oct 2024

Original Article

Cathode Electrode Active Material Properties Evaluation for Lithium-Ion Batteries

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Received: 06 August 2024 Revised: 09 September 2024 Accepted: 24 September 2024 Published: 14 October 2024

Abstract - *The major element that hinders the performance of batteries is the active element of the cathode electrode. There has been an effort to offer and study oxide composites centered on transition metal elements, with a target on those compounds that accommodate large movements of Li^+ ions such that during redox reactions, energy can be transferred. Nevertheless, these lithium-insertion composites should satisfy physical, mechanical, and electrochemical properties. Consequently, material properties evaluation for lithium-ion batteries cathode electrode active material with high nickel content is presented. The properties, namely, hardness, tensile strength, compressive strength, electrical resistivity, density, and cost, are analyzed with the assistance of CES EduPack Software. Understanding $Li(Ni_{1/2}Co_{1/5}Mn_{3/10})O_2$ cathode material properties is essential to predicting and simulating the electrochemical performance of lithium-ion batteries with high reliability.*

Keywords - *Batteries, Active material properties, $Li(Ni_{1/2}Co_{1/5}Mn_{3/10})O_2$, Bubble chart.*

1. Introduction

Renewable energy sources, unlike fossil fuels, are more difficult to store [1]. Energy storage devices, such as batteries, are critical for storing energy for later consumption and returning it to the grid when necessary. The need to address climate change has accelerated the development of batteries to reduce carbon emissions and boost the use of renewable energy [2-3]. Because of its ability to store energy, lithium-ion batteries have proven to be effective secondary energy sources for powering electronic equipment. However, satisfying the energy demands of hybrid electric vehicles necessitates increased energy density [4], and there are still obstacles to overcome before lithium-ion batteries can fully dominate high-performance automotive and portable electronics. Improving the positive electrode, negative electrode, and electrolyte materials can help improve battery performance [5, 6]. Metal oxides, notably those based on Ni, Mn, Co, Cu, and Fe, show promise as cathode active materials. These oxides can store energy by redox processes and the incorporation of lithium composites [7, 8]. Modern positive electrode materials for lithium-ion batteries include lithium metal oxides, olivines ($LiFePO_4$), lithium oxides, and vanadium oxides [9]. The specific category determines the ion migration paths and activation energy that control the movement of lithium ions within the electrode material [10]. From a materials standpoint, active materials with low cobalt concentration, such as NMC (nickel manganese cobalt), are regarded as promising for future generation Li-ion battery-positive electrodes. Reducing cobalt dependency is critical due to extraction issues and major cost concerns, whereas nickel-loaded options provide decreased reliance on cobalt while maintaining high capacity. Furthermore, NMC with low nickel concentration is widely utilized in electric vehicles due to its superior properties such as power capacity, chemical stability, high-rate capacity, thermal strength, and long cycle life. Substituting nickel-loaded NMC improves capacity significantly because higher nickel content allows for greater lithium extraction while maintaining structural integrity [11]. Layered oxides comprising nickel and cobalt are extensively investigated materials for lithium-ion batteries, providing better strength across the peak voltage spectrum. However, cobalt's toxicity and limited availability provide substantial hurdles for large-scale production. Manganese is a low-cost alternative with excellent rate capabilities and thermal stability, but it has a short cycle life. As a result, mixtures of nickel, manganese, and cobalt are typically used to attain the optimum characteristics while minimizing deficits. CES EduPack takes a systematic and coordinated approach to material selection, giving significant data and tools for evaluating the sustainability of future products and technology [12]. This is especially crucial for engineering education and training [13]. The platform's available databases allow for educated decision-making about items in a variety of specialist fields [14]. CES EduPack is extremely useful for studying electric motors and batteries. It makes it easier to visualize performance characteristics using charts and essential property data, offering light on why Li-ion batteries and Nd-based magnets are preferred over other technologies. The

Elements database provides information on important materials such as lithium, cobalt, and rare earths, including the primary mining areas. In the world of electric car batteries, lithium-ion technology reigns supreme, with alternative systems such as NiMH used to a lesser amount. Cobalt and graphite are frequently employed alongside lithium in these batteries. At the same time, rare earth metals, particularly praseodymium, neodymium, terbium, and dysprosium, play critical roles in high-performance magnets and electronic sensors for the regular car sector. These elements find use in a variety of automobile components, including seat adjustments, starting motors, car stereo speakers, and brake systems. Figure 1 depicts why Li-ion batteries are ideal for electrochemical energy storage in automobiles, displaying their high energy storage and power delivery capacities per kilogram. This visual representation demonstrates their efficiency and appropriateness for use in electric vehicles.

The ideal material for multilayer cathodes is nickel-rich low-cobalt with over 90% Ni due to its high discharge capacity greater than 210 $mAhg^{-1}$, energy density greater than 740$Whkg^{-1}$, structural stability and other features [15]. Because of its large capacity, lithium-ion batteries with a high percentage of nickel cathode have recently gained attention. To offer enough context on the topic, existing research inputs are highlighted. Joe et al. studied the mechanical properties of cathode materials for lithium-ion batteries. Measurements of the mechanical properties of lithium-ion battery cathode materials are summarized from the literature, as well as the spectrum of experimental methods utilized to determine them. Dimensional changes caused by charge and discharge are compared for active materials with spinel, olivine, and layered atomic structures.

The sensitivity of indentation hardness, Young's modulus, and fracture strength to grain size, porosity and state of charge history is thoroughly examined and addressed. This approach enables the determination of microstructural features that determine the mechanical properties of lithium-ion battery cathode materials [16]. Philip et al. investigated the design of cathodes and active materials for solid-state batteries. Several difficulties that prevent solid-state batteries from outperforming today's lithium-ion batteries with liquid electrolytes are identified.

One significant problem is the development of cathode-active materials that are compatible with the superionic solid electrolytes of interest. This perspective provides a summary of the required qualities and potential obstacles for inorganic cathode active materials used in solid-state batteries, as well as descriptions of cutting-edge solutions. In particular, the issue of tailoring cathode active materials is structured into challenges arising on the cathode-, particle-, and interface level related to the microstructural, mechanical, and chemical interplay of cathode active materials with solid electrolytes.

Finally, guidelines for future cathode active materials development for solid-state batteries are proposed [17]. A comparative analysis of the electrochemical and physical characteristics of positive electrodes used in lithium-ion batteries was published by Julien et al. Based on the dimensionality of the Li+ ion motion, electrode materials can be divided into three classes: spinel frameworks, layered transition-metal oxides, and olivine. With a focus on synthesis challenges, electrochemical stability, faradaic performance, and security concerns, their benefits and drawbacks are contrasted [9].

Cho et al. conducted a study on the issues and solutions pertaining to Ni-rich cathode-based Li-ion batteries from two research perspectives, utilizing both computational and experimental studies. A summary was provided of the experiments and computational techniques for performance enhancement employing different approaches, including doping, coating, washing, and single crystalline cathodes, to address this issue. The outcomes of the experiments and computations may speed up the future search for Ni-rich cathode materials and offer new perspectives on the mechanisms underlying a variety of phenomena [18].

Numerous studies have been conducted to get a better knowledge of the physical, mechanical and electrochemical processes within various battery components. Nevertheless, phase transitions, cation mixing issues, structural instability, and decreased electrochemical performance plague the high-content nickel cathodes. These problems raise the possibility of battery combustion and lead to low cycle efficiency. Hence the introduction of CES EduPack Software for the lithium-ion battery analysis. CES EduPack is used in this work to evaluate the material properties of the active material of the lithium-ion battery cathode. Compressive strength, tensile strength, hardness, electrical resistivity, density, and cost are all studied using software-generated material property charts, along with other parameters. The study's goal is to obtain insights into the positive active material features of $Li(Ni_{1/2}Co_{1/5}Mn_{3/10})O_2$, which are critical for accurately forecasting and simulating the electrochemical performance of lithium-ion batteries.

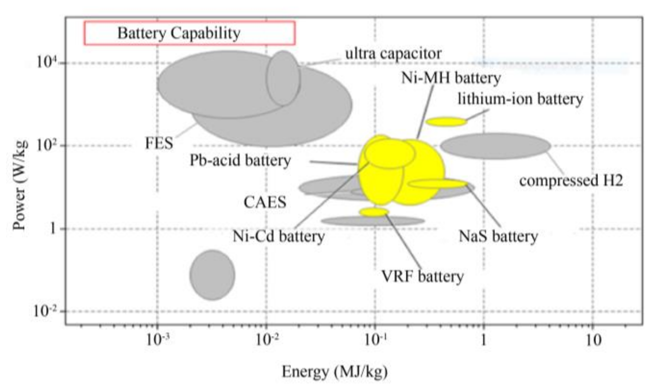

Fig. 1 Overview of performance chart of different batteries

Table 1. The physical state of the lithium-ion battery

No	Item	Parameter	Note
1.	Cell Thickness	6.0 mm	
2.	Cell Width	50 mm	
3.	Cell Height	60 mm	
4.	Cell Weight	38 g	
5.	Appearance	Pouch	

2. Materials and Methods

A layered lithium NMC oxide cathode electrode of a pouch cell, BZ605060, containing nickel, 0.5%, manganese, 0.3% and cobalt, 0.2 concentrations, was used in this study. The three composite active materials, nickel, manganese and cobalt, were analyzed and compared with the aid of material property charts. The CES EduPack Software is set to advance to give a more detailed property of any material that is selected, such as general property, mechanical property, electrical property, thermal property, optical property, eco property, durability, material processing and recycling. Regarding this study, tensile strength, hardness, compressive strength, density, electrical resistivity and cost were considered. The Software obtains bubble charts of the three NMC active materials, with numerical values of each property in consideration as generated by the charts, thus simplifying material property analysis.

2.1. Experimental

A coating comprising a dispersion of polycrystalline $Li(Ni_{1/2}Co_{1/5}Mn_{3/10})O_2$ (Sigma-Aldrich), Super C65 (Timcal) with an exchange surface area of 65 m²/g, and VGCF-H carbon conductive additive from Showa Denko materials Co. was applied to create the cathode electrode based on NMC. A 90:3:3:4 weight ratio of PolyVinylidene Fluoride (Kureha KF 7208) was employed as a binder. The coating was placed on aluminum foil. The same method was used to prepare the graphite-based anode electrode, which was coated on copper foil and consisted of spherical graphite mixed with CMC-7H3SF (Aqualon Ashland) and SBR 2 (BASF Master Emaco) binders (sodium carboxymethyl cellulose and styrene butadiene rubber) in a weight ratio of 97.2:1.4:1.4. Both electrodes were prepared using an internal laboratory process. The components were mixed using a planetary mixer, and the cathode was dissolved in N-methyl pyrrolidone (NMP) from Sigma Aldrich, while the anode was dissolved in deionized water. The current collectors were then treated with the slurry. To coat the two electrodes, a specially designed reverse roll coater with a 1.4 m drying oven was placed in a dry room. The electrodes were then calendared to get the required porosity. The loading of the anode was 11.0 mg/cm², while the loading of the cathode electrode was 17.9 mg/cm². For the cathode and anode electrodes, the porosity values were 32% and 34%, respectively. These loadings translate into 3.21mAh/cm² and 3.69mAh/cm², respectively, when the projected reversible capacity is considered. This yields a direct anode/cathode ratio of 1.2. The polypropylene (PP) monolayer, Celgard 2400, with a thickness of 25 µm, serves as the separator. The electrolyte utilized, which was supplied by Sigma-Aldrich, is made up of a 1:1:1 weight ratio of 1M lithium hexafluorophosphate (LiPF6) for Ethylene Carbonate (EC), Ethyl Methyl Carbonate (EMC), and Dimethyl Carbonate (DMC). The electrolyte's purity limit is 5 parts per million of H2O and 10 parts per million of HF. A large excess of electrolyte is employed to guarantee complete wetting of the electrodes and avoid electrolyte famine.

2.1.1. Design

In the design, the tested electrodes-graphite for the anode and $Li(Ni_{1/2}Co_{1/5}Mn_{3/10})O_2$ for the cathode are arranged in a pouch cell arrangement. As shown in Figure 2, a lithium foil reference electrode is placed between the cathode and separator, which is covered with a second separator to prevent short circuits. A nickel tab is welded to the anode, and an aluminum tab is ultrasonically welded to the cathode. The pouch cells are built in a dry room with a -23°C dew point and placed within a glove box that is filled with argon and electrolyte. The pouches are partially vacuum sealed before sealing, and a heat sealer is used to secure the assembly. The anode electrode has a surface area of 13.69 cm² (3.7x3.7), whereas the cathode electrode C_{sa} has a surface size of 11.56 cm² (3.4x3.4). These measurements are chosen to minimize the discrepancy and ensure adequate coverage of the cathode electrode by the anode electrode. However, because of the creation of the solid electrolyte interface (SEI) caused by the lithium consumed at the anode electrode during early lithiation, this disparity results in an increase in invariable capacity. This disparity in area causes the cathode to be used less, which at the cell scale results in an electrode capacity ratio of 1.4 rather than the intended direct anode/cathode ratio of 1.2. For $Li(Ni_{1/2}Co_{1/5}Mn_{3/10})O_2$ and graphite, the estimated exchange surface areas (ESA) for this cell configuration are roughly 21.85 m² and 22.16 m², respectively. (as shown in Table 2)

Table 2. Applied parameters for the cathode and anode selection

Parameters	Values			
	Graphite	Li $(Ni_{1/2}Co_{1/5}Mn_{3/10})O_2$	Source	Error
S_g (m^2)	11.55e-4	10.34e-4	calculated	-
I_0 (A) during Pulse	4.5e-4	5.4e-4	calculated	-
V_M (m^3. mol^{-1})	5.21e-6	11.75e-6	calculated	-
r_{50} (m)	8.48e-6	7.3e-6	measured	±1.7µm
S_{AM} (m^2)	21.78e-4	21.63e-4	calculated	-
L (m)	73e-6	67e-6	measured	±1µm

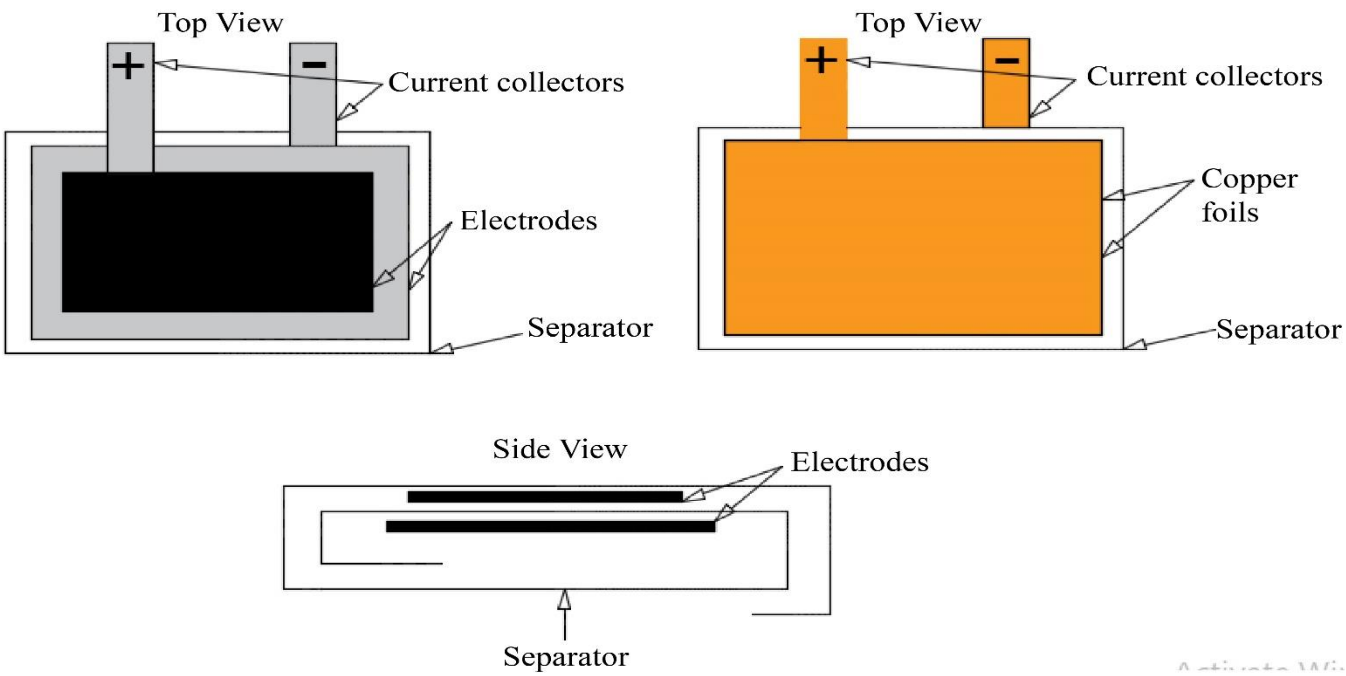

Fig. 2 Schematic showing the top and side views of a three-electrode pouch cell design

3. Results and Discussions

The hardness and tensile strength chart for the active materials is shown in Figure 3a. According to the chart, nickel has a lower hardness of 170 HV and a greater tensile strength of 445 MPa, while manganese has a higher hardness of 220 HV and cobalt has a higher tensile strength of 840 MPa.

Figure 3b shows the chart of hardness and compressive strength for the active materials. According to the chart, nickel has a lesser compressive strength of approximately 110 MPa and a harder surface of about 170 HV. In comparison, cobalt has a greater strength of around 500 MPa and manganese has a higher hardness of about 220 HV.

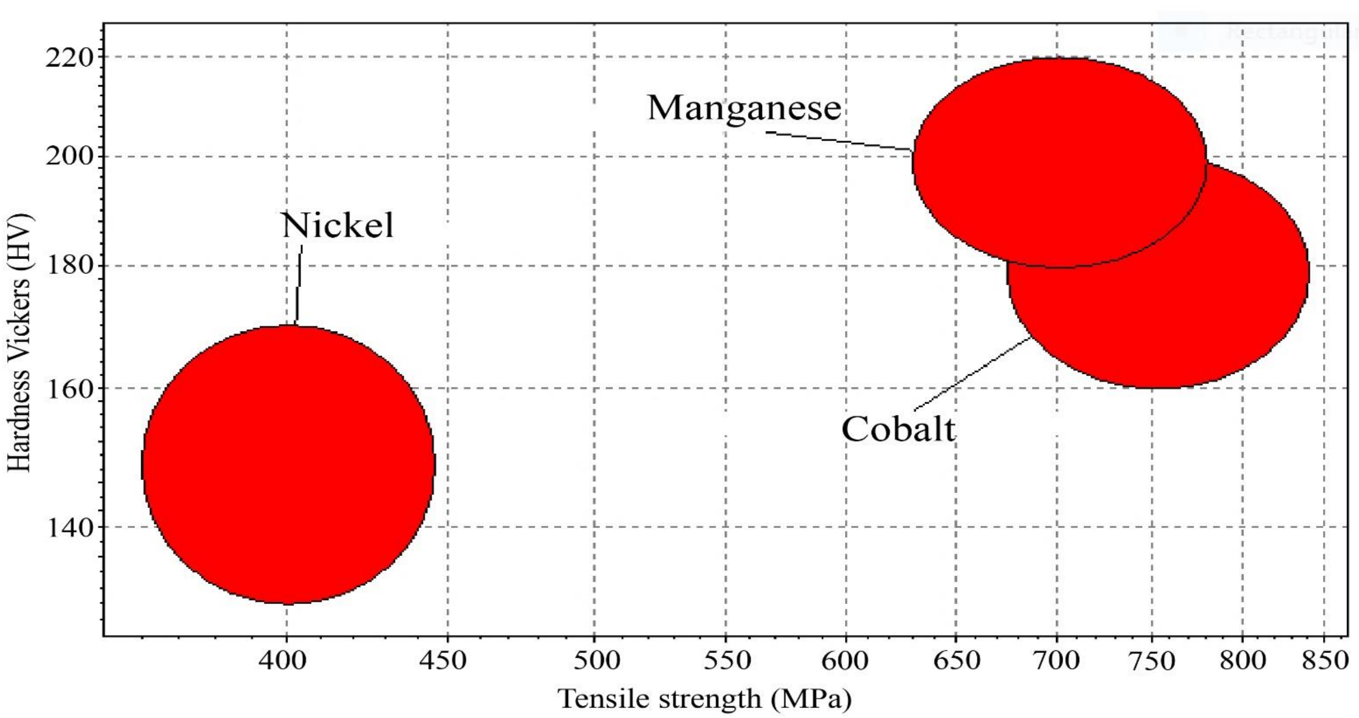

Fig. 3 (a) Chart of hardness against tensile strength for Ni, Mn and Co

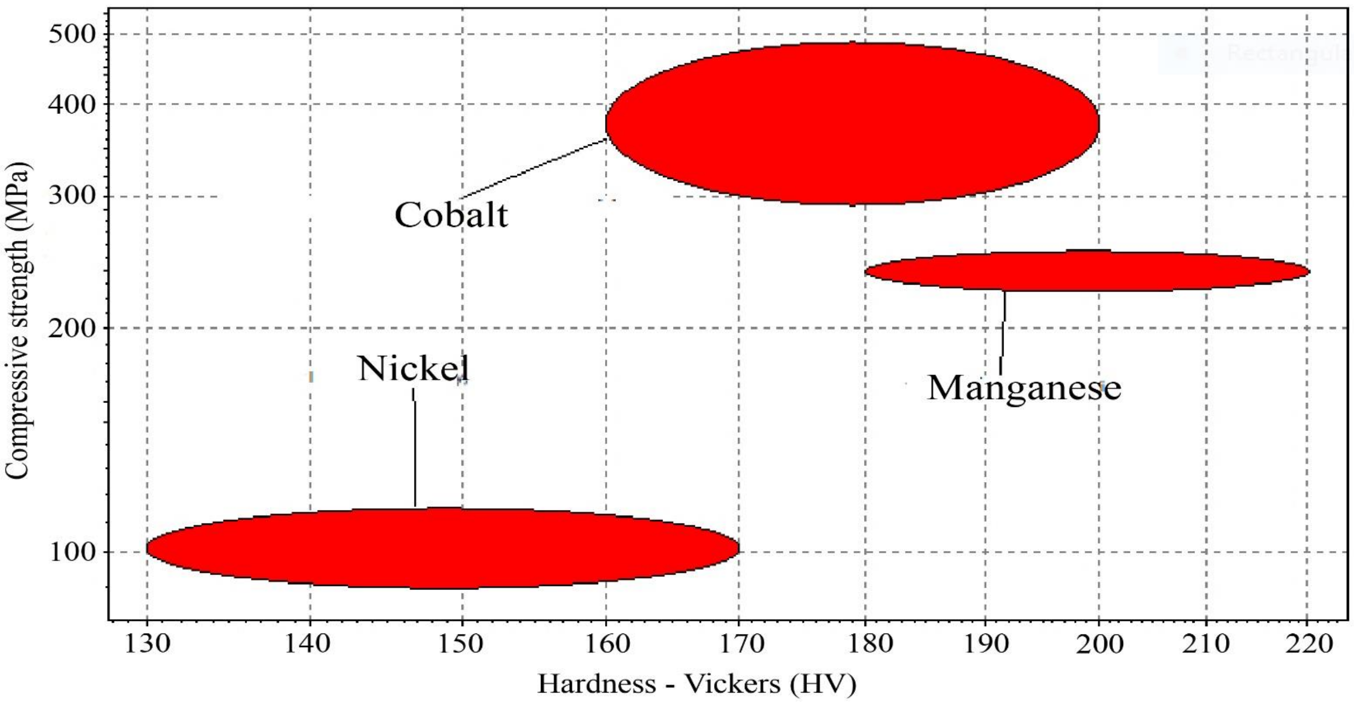

Fig. 3 (b) Chart of hardness against compressive strength for Ni, Mn and Co

Figure 4a presents the chart of density and price for the active materials. From the chart, nickel (8950 kg/m^3, NGN6000) and cobalt (8900 kg/m^3, NGN5200) are seen to have a higher density and price, whereas manganese (7500 kg/m^3, NGN350) shows a lower density and price. The hardness and electrical resistivity chart for the active materials is displayed in Figure 4b. According to the chart, nickel has a lower electrical resistivity of 9 ohm/cm and a lower hardness of 170 HV, while manganese has a higher hardness of 220 HV and a lower electrical resistivity of 150 ohm/cm. Cobalt, on the other hand, has a higher hardness of 200 HV and a lower electrical resistivity of 8 ohm/cm.

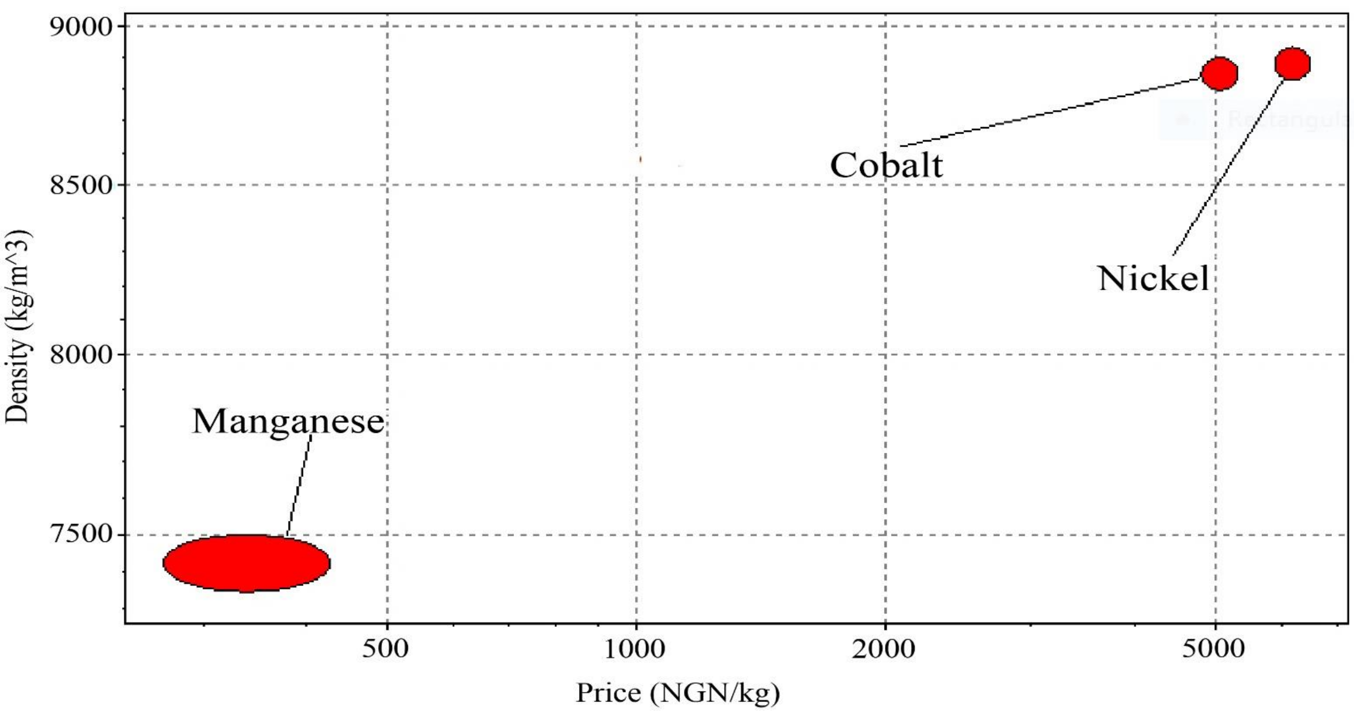

Fig. 4 (a) Chart of density against price for Ni, Mn and Co

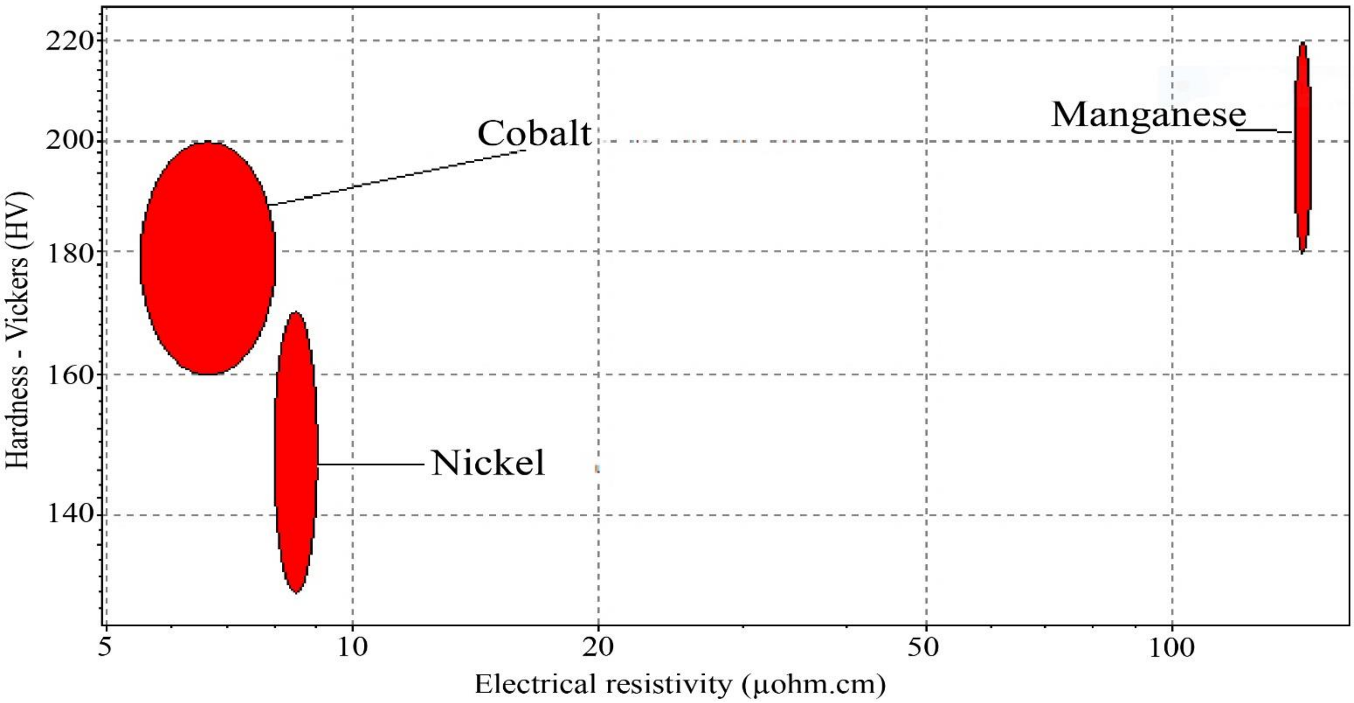

Fig. 4 (b) Chart of hardness against electrical resistivity for Ni, Mn and Co

According to the data, manganese is the best material in terms of cost and hardness; cobalt is the greatest option in terms of conductivity, tensile strength, and compressive strength; and nickel is the best material in terms of energy density. The generated results align with the comprehensive material properties as documented in the literature and supplementary documents, indicating consistency and agreement between the simulation data and the referenced sources. The essence of these analyses includes but is not limited to, a brief synopsis of material qualities for the purpose of comparing various possibilities, a deeper comprehension of material decisions and their implications, and a review of the complete product life cycle at the developmental and design stages.

4. Conclusion and Recommendations

This study presented a new strategy for assessing the active material properties of $Li(Ni_{1/2}Co_{1/5}Mn_{3/10})O_2$ cathode electrodes in lithium-ion batteries. These properties were examined with the aid of CES EduPack software, confirming three crucial benefits, though not limited: a quick overview of material properties to compare different options, understanding of material decisions and their consequences, and examination of the entire product life cycle at the developmental and design stages. The obtained results agree with most previously reported values for the referenced cathode electrode. These findings are essential to predicting and simulating the electrochemical performance of lithium-ion batteries with authenticity. This evaluation method can be used to determine the viability of composite or alternative materials with high nickel cathode content and the mechanism of performance enhancement prior to starting any experiment.

The importance of this active material property evaluation to cathode material industries interested in layered oxides cannot be overstated. In order to validate fracture and failure analysis in cathode electrode active material composites in lithium-ion batteries, future research will concentrate on extensive experimental measurements.

Acknowledgements

I would like to thank Fordland Engineering for their efforts in helping to develop the technical and experimental solutions.

References

[1] Manh-Kien Tran et al., “Comparative Study of Equivalent Circuit Models Performance in Four Common Lithium-Ion Batteries: LFP, NMC, LMO, NCA,” *Batteries*, vol. 7, no. 3, pp. 1-15, 2021. [CrossRef] [Google Scholar] [Publisher Link]

[2] Manh-Kien Tran et al, “Environmental and Economic Benefits of a Battery Electric Vehicle Powertrain with a Zinc-Air Range Extender in the Transition to Electric Vehicles,” *Vehicles*, vol. 2, no. 3, pp. 1-15, 2020. [CrossRef] [Google Scholar] [Publisher Link]

[3] Manh-Kien Tran et al., “A Review of Range Extenders in Battery Electric Vehicles: Current Progress and Future Perspectives,” *World Electric Vehicle Journal*, vol. 12, no. 2, pp. 1-16, 2021. [CrossRef] [Google Scholar] [Publisher Link]

[4] Kevin G. Gallagher et al., "Quantifying the Promise of Lithium-Air Batteries for Electric Vehicles," *Energy & Environmental Science*, vol. 7, pp. 1555-1563, 2014. [CrossRef] [Google Scholar] [Publisher Link]

[5] Andrzej Lewandowski, and Agnieszka Świderska-Mocek, "Ionic Liquids as Electrolytes for Li-Ion Batteries: An Overview of Electrochemical Studies," *Journal of Power Sources*, vol. 194, no. 2, pp. 601-609, 2009. [CrossRef] [Google Scholar] [Publisher Link]

[6] Naoki Nitta, and Gleb Yushin, "High-Capacity Anode Materials for Lithium-Ion Batteries: Choice of Elements and Structures for Active Particles," *Particle & Particle Systems Characterization*, vol. 31, no. 3, pp. 317-336, 2013. [CrossRef] [Google Scholar] [Publisher Link]

[7] Hyunchul Kim et al., "New Insight into the Reaction Mechanism for Exceptional Capacity of Ordered Mesoporous SnO_2 Electrodes via Synchrotron-Based X-ray Analysis," *Chemistry of Materials*, vol. 26, no. 22, pp. 6361-6370, 2014. [CrossRef] [Google Scholar] [Publisher Link]

[8] Hyunchul Kim et al., "Comparative Study of Bulk and Nano-Structured Mesoporous SnO_2 Electrodes on the Electrochemical Performances for Next Generation Li Rechargeable Batteries," *Journal of Power Sources*, vol. 413, pp. 241-249, 2019. [CrossRef] [Google Scholar] [Publisher Link]

[9] Christian M. Julien et al., "Comparative Issues of Cathode Materials for Li-Ion Batteries," *Inorganics*, vol. 2, no. 1, pp. 132-154, 2014. [CrossRef] [Google Scholar] [Publisher Link]

[10] John B. Goodenough, "Design considerations," *Solid State Ionics*, vol. 69, no. 3-4, pp. 184-198, 1994. [CrossRef] [Google Scholar] [Publisher Link]

[11] Yuanli Ding et al., "Automotive Li-Ion Batteries: Current Status and Future Perspectives," *Electrochemical Energy Reviews*, vol. 2, pp. 1-28, 2019. [CrossRef] [Google Scholar] [Publisher Link]

[12] Mike Ashby, Didac Ferrer, and Jennifer Bruce, "*Materials and Sustainable Development*," Engineering Department, Cambridge University, UK, pp. 1-45, 2021. [Google Scholar] [Publisher Link]

[13] Mike Ashby, Tim Davies, and Stéphane Gorsse, "*CES EduPack DB for Bulk Functional Materials*," Granta Teaching Resources, 2015. [Google Scholar] [Publisher Link]

[14] Nguyen, Ruby Thuy et al., "Imholte A Market-Oriented Database Design for Critical Material Research," *Clean Technologies and Recycling*, vol. 1, no. 1, pp. 34-39, 2021. [CrossRef] [Google Scholar] [Publisher Link]

[15] Yu Xia et al., "Designing Principle for Ni-Rich Cathode Materials with High Energy Density for Practical Applications," *Nano Energy*, vol. 49, pp. 434-452, 2018. [CrossRef] [Google Scholar] [Publisher Link]

[16] Joe C. Stallard et al., "Mechanical Properties of Cathode Materials for Lithium-Ion Batteries," *Joule*, vol. 6, no. 2, pp. 984-1007, 2022. [CrossRef] [Google Scholar] [Publisher Link]

[17] Philip Minnmann et al., "Designing Cathodes and Cathode Active Materials for Solid-State Batteries," *Advanced Energy Materials*, vol. 12, no. 35, pp. 1-18, 2022. [CrossRef] [Google Scholar] [Publisher Link]

[18] Hyukhee Cho et al., "A Review of Problems and Solutions in Ni- Rich Cathode-Based Li-Ion Batteries from Two Research Aspects: Experimental Studies and Computational Insights," *Journal of Power Sources*, vol. 597, 2024. [CrossRef] [Google Scholar] [Publisher Link]