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Correlative Survey of Blended $LiCoO_2$ and $LiMn_2O_4$ Cathode Materials for Lithium-ion Batteries

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Abstract. *We employed the lithium-ion battery model in Multiphysics to simulate the electrochemical characteristics of lithium-ion batteries. These batteries consist of a cathode mixture comprising* $LiCoO_2$ *and* $LiMn_2O_4$*, as well as quasi-graphite anode. Our simulations successfully replicated the discharge profiles of both unblended and blended cathodes across different current rates, aligning with results obtained from experiments. The energy and power densities of the blended cathode framework were regulated by adjusting the mix ratio in the simulation model. Additionally, the blended electrodes of* $LiCoO_2$ *and* $LiMn_2O_4$ *demonstrated an above-average electrochemical performance, combining the characteristics of the two active materials.*

Keywords: Lithium-ion Battery; Blended Cathode Active Materials; Simulation; Experiment.

Introduction

This study involves a systematic investigation of two cathode materials; $LiCoO_2$ and $LiMn_2O_4$, to establish connections or relationships between the blended systems of the electrode materials. Because of their better energy density and similar calendar and cycle lives, lithium-ion batteries have supplanted nickel-metal hydride batteries in a wide range of electronic devices and electric cars [1]. The interdisciplinary aspect of finding cathode materials for lithium-ion batteries was highlighted by Huang. Based on his deep understanding of chemical structure and bonding, Professor John B. Goodenough's early solid-state physics research provided the fundamental ideas underpinning lithium cobalt oxide, lithium manganese oxide, and $LiFePO_4$.The author highlighted that, with the rapid advancement of rechargeable batteries, this interdisciplinary approach has expanded to include engineering, information sciences, and even artificial intelligence [2]. There is hope that further study and technical advancement will soon result in better solutions, despite current problems including energy density and safety issues with batteries. However, to match the range needs of conventional internal combustion engine vehicles, Li-ion battery energy density improvements must continue. High energy density new electrode active materials can be developed to do this [3-4]. Researchers have been investigating the creation of blended electrode active materials in an effort to meet the stringent standards of lithium-ion batteries for electric automobiles and other household electronics. Blended materials often have higher energy densities compared to traditional intercalation materials like graphite. This means they can store more energy per unit of mass or volume, which is crucial for increasing the energy capacity of batteries. Among them, $LiMn_2O_4$ and $LiNiMnCoO_2$ have garnered significant attention due to their combined ability to provide high energy densities and excellent rate capability. However, $LiMn_2O_4$ has limitations, such as low energy density and poor cycling stability at elevated temperatures [5]. To overcome these drawbacks, an alloyed electrode system integrates $LiMn_2O_4$ with $LiNiMnCoO_2$ cathode active material possessing a high energy density. This allows the battery to retain additional energy, resulting in extended operational durations and heightened power density [6-8].

The elements influencing blended systems' advantageous electrochemical performances have been the subject of numerous prior studies [9-10]. However, figuring out the ideal mix ratio and blend chemistry alone by trial and error can be difficult and expensive. Within this framework, simulation techniques offer a productive means of forecasting the electrochemical behavior of various mixes. Paul et al. conducted a study that compared coin cells' experimental and simulated galvanostatic discharge performances. These cells contained mixed cathodes with varying proportions of $Li_yMn_2O_4$ and $Li_yNi_{0.8}Co_{0.15}Al_{0.05}O_2$, covering a wide range of discharge rates. The researchers assumed equal thicknesses of the two active systems and their blends, as well as equal electrolyte volume ratios. Nevertheless, they were unable to carry out in-depth life investigations on the cells since they were using half-cells with Li metal as the negative electrode [11–12]. In this work, we utilized the Multi-physics lithium-ion battery model to simulate the electrochemical characteristics of refined and blended $LiMn_2O_4$ and $LiCoO_2$ cathodes. We next compared the results of these models to experimental data collected from pouch-full cells running at 25°C. Gaining knowledge about the cathode blend's lifetime and performance was the main goal of our research. Solid-phase diffusion and reaction kinetics are two examples of the physical phenomena that must be integrated into a multiphysics model in order to accurately represent the electrochemical properties of lithium-ion batteries.

Theoretical Background

A battery, which has one or more electrochemical cells inside of it, serves as an energy storage device. Through electrochemical processes, it converts the chemical energy contained in its active components to electrical energy [13]. Anode, cathode, and electrolyte are the main components of a battery. A separator and current collector are the auxiliary parts that complete the battery. The next generation of lithium-ion batteries is being developed by researchers from government laboratories, agencies, and university institutions with the goal of improving characteristics such as charge/discharge capacity. However, battery creation can occasionally become more of an art than a simple science due to the complex interactions between materials science, physics, and engineering. The problem is that scientists and engineers are limited in the chemical elements and configurations they can use to create batteries. Finding the elements that work best with lithium-ion electrodes has been the subject of extensive research and continuous efforts [14]. While commercially available cathode active materials such as lithium nickel cobalt aluminum oxide ($LiNiCoAlO_2$ or NCA), lithium iron phosphate ($LiFePO_4$ or LFP), lithium nickel manganese cobalt oxide ($LiNiMnCoO_2$ or NMC), lithium manganese oxide ($LiMn_2O_4$ or LMO), and lithium cobalt oxide ($LiCoO_2$ or LCO) are used, anode active materials like lithium titanate ($Li_4Ti_5O_{12}$), graphite, and amorphous carbon are also employed [6-8]. For example, Zheng et al. conducted a study on a comprehensive understanding of electrode thickness effects on the electrochemical performances of Li-ion battery cathodes composed of $LiMn_2O_4$ and $Li(Ni_{0.6}Co_{0.2}Mn_{0.2})O_2$. These materials were chosen to address their respective limitations. Through experiments and simulations, it was shown that the addition of $Li(Ni_{0.6}Co_{0.2}Mn_{0.2})O_2$ to $LiMn_2O_4$ reduced the dissolution of Mn^2 ions, resulting in a 21% suppression of capacity fade in $LiMn_2O_4$ after 100 cycles. Consequently, the cycle performance of $LiMn_2O_4$ as an active material improved when combined with $Li(Ni_{0.6}Co_{0.2}Mn_{0.2})O_2$ as the cathode active material [15]. In another study carried out by K. Hyun-Soo, a blend of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ and $Li_{1.1}Mn_{1.9}O_4$ in a 1:1 weight ratio was investigated. The blended cathode exhibited favorable capacity retention compared to pure $Li_{1.1}Mn_{1.9}O_4$. The researchers concluded that the addition of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ enhanced the capacity retention of $Li_{1.1}Mn_{1.9}O_4$. In addition to the aforementioned research, a large body of literature has been written about hybrid cathode systems that combine several cathode active materials in an effort to produce harmonious characteristics in lithium-ion batteries. Due to its potential to be a very thermally stable cathode material compared to other commercially available layered oxides, $LiMn_2O_4$ has drawn a lot of study attention [16]. But it's important to recognize that $LiMn_2O_4$ has low energy density as well [17–18]. There hasn't been much research done on the complementary impacts of two refined cathode materials, $LiMn_2O_4$ and $LiCoO_2$, on one another in a cathode system. $LiCoO_2$ has shown to be a valuable cathode material because of its noteworthy characteristics, which include high energy density, voltage stability, cycling efficiency, and rate flexibility. These qualities have established it as a favored selection in a range of applications where these characteristics are paramount. Hence, we investigated two blended positive electrode, comprising a mixture of $LiMn_2O_4$ and $LiCoO_2$.

Materials and Methods

Experimental

In this study, we utilized two cathode active materials: $LiMn_2O_4$ obtained from Soundon New Energy Co., Ltd., China, and $LiCoO_2$ obtained from Shandong Gelon Lib Co., Ltd., China. To conduct experimental investigations on the electrochemical properties, we fabricated 906090 pouch-type cells. These cells had cathodes with three different mix ratios of $LiMn_2O_4$ and $LiCoO_2$, while the anode was made of artificial graphite from Shenzhen Sinuo Industrial Development Co. Ltd. The cathode composition of the electrodes consisted of 92 wt% blended active materials, 4 wt% conductive additive (Soundon New Energy Co., Ltd., China), and 4 wt% polyvinylidene fluoride (PVDF) from Kureha Corporation, Japan, serving as a binder. For the preparation of the electrode slurry, N-methyl pyrrolidone (NMP) from Sigma Aldrich, USA, was used as the solvent. The cathode slurry was applied onto 15µm-thick aluminum foil (Shandong Linxu Materials Co., Ltd., China) using the doctor blade procedure, followed by drying at 120°C for 60 minutes to remove the solvent. The electrodes were punched, and then dried again under vacuum at 60°C to get rid of any last traces of water and NMP solvent. SEM, specifically the Phenom Prox from the Netherlands, was used to analyze the surface morphology of the electrodes.

Three distinct blended cathodes were made, each with a density that was roughly equal. The electrode thickness and porosity were both meticulously regulated to be equivalent in order to guarantee comparable liquid phase outcomes within the cells.

We used aluminum and polypropylene separators from Dongguan Mochuang New Energy Materials, China, for the assembly of the pouch cells. The liquid electrolytes were composed of 1.15 M $LiPF_6$ in a mixture of ethylene carbonate, ethylmethyl carbonate, and diethyl carbonate (3/7 by volume) obtained from Dongguan Tianfeng Power Material Co., Ltd., China. After construction, the cells were aged for 16 hours and then subjected to cycling at a constant current (CC) of 0.1C for both the charging and discharging processes. This initial cycling step served as a formation process and was conducted using a charge/discharge cycler from

Dongguan ZhengRui Automatic Equip. Techn. Co., Ltd., China, at a temperature of 25°C. Following the formation step, a stabilization process was performed for three cycles at a 0.3C rate. To assess the rate capability, we tested three cells for each cathode composition at various current rates: 0.3C, 0.6C, 1C, 2C, 4C, 6C, 8C, and 10C, with each rate maintained for three cycles. The discharge processes at different C rates were followed by a constant current/constant voltage (CC/CV) charging at a 0.3C rate. In all cases, we applied an upper limited charge voltage of 4.2 V and a lower cut-off voltage of 3.0 V. To establish a reference rate (0.3C), the capacities of all the cells were normalized to their respective 0.3C capacities. The electrochemical reactions that occur during charge/discharge process in the Lithium-ion cell is as shown in **Figure 1**.

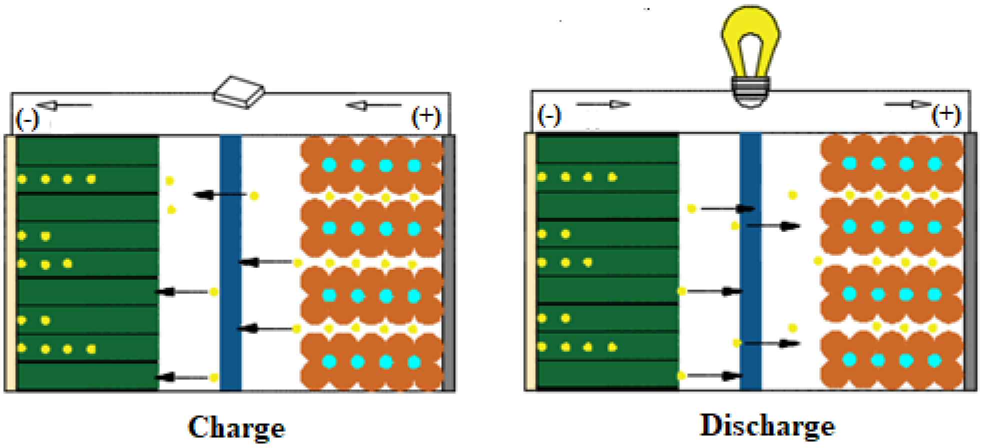

Figure 1. Cross section of Li- ion cell describing the electrochemical reactions

Results and Discussion

Determination of Morphology

The morphology of the blended and unblended positive electrodes was examined in the study using scanning electron microscopy (SEM), which gave important insights into the structural properties and particle configurations within the cathode. The micrographs shown in **Figure 2** showed the unblended electrode next to the blended electrode that had a weight ratio of 5:5 between $LiMn_2O_4$ and $LiCoO_2$. The two active materials were evenly mixed within the electrode structure, as seen by the blended electrode's SEM image. This consistency is the outcome of the electrodes' wet thicknesses and loading densities being carefully controlled, which guaranteed that the cathode's composition would not change over the course of the investigation. The gaps between the $LiCoO_2$ particles were effectively filled with $LiMn_2O_4$ particles and carbon black conductive material, leading to a well-dispersed and homogenous mixture of active materials.

The blended electrode demonstrated effective interaction between the conductive additives and the active components by eliminating inter-particle gaps and attaining enhanced dispersion. Better charge transfer and ion diffusion kinetics were encouraged by this improved contact, which improved the cathode's overall electrochemical performance. A cathode with harmonic

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qualities was produced by combining $LiMn_2O_4$ and $LiCoO_2$ in a weight ratio of 5:5, which addressed the drawbacks of each material separately and enhanced battery performance, capacity retention, and cyclability.

The study's methodology is further supported by the quantitative measurements of the electrode properties, such as loading densities and thicknesses, shown in **Table 1**. We were able to fairly and accurately compare the various positive electrode compositions under study by maintaining uniformity in the electrode composition and managing the electrode's wet thickness.

All things considered, the SEM analysis of the electrode morphology was really helpful in comprehending the structural characteristics and particle distribution of the cathode. This information is essential for creating cathode materials with enhanced electrochemical behavior and lifespan, as well as maximizing the performance of Li-ion batteries.

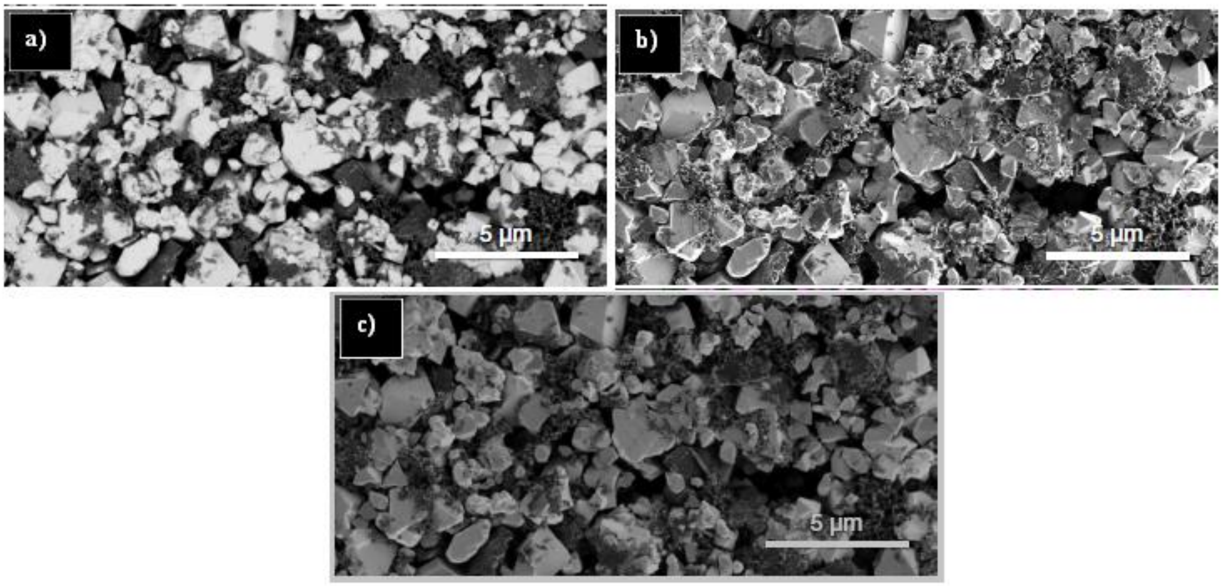

Figure 2. SEM image of electrodes consisting (a) unblended $LiMn_2O_4$ (b) unblended $LiCoO_2$ and (c) blended electrodes consisting 5:5 weight ratio of $LiMn_2O_4$ and $LiCoO_2$.

Performance Rate

Figure 3a in the study presents a comparison of the low-rate discharge profiles (0.3C rate) of three positive electrodes: unblended $LiMn_2O_4$, unblended $LiCoO_2$, and the blended cathode with a 5:5 weight ratio of $LiMn_2O_4$ and $LiCoO_2$. Notably, the blended cathode in this study exhibits identical initial and final discharge characteristics to that of unblended $LiCoO_2$ at the low-rate discharge stage. This suggests that, at this point, the $LiCoO_2$ component is mostly responsible for the current delivery. In the unblended $LiMn_2O_4$ electrode system, however, an increased elevation is seen at cell output potential difference values lower than 3.8 V. This implies that $LiMn_2O_4$ electrochemical behavior manifests itself in this potential range. The distinct discharge characteristics observed in this area suggest that $LiMn_2O_4$ plays a major role in the blended cathode's electrochemical performance.

The discharge characteristics for the three cathodes; unblended $LiMn_2O_4$, unblended $LiCoO_2$, and the blended cathode with a 5:5 weight ratio are directly compared at a higher rate (4C rate) in **Figure 3b**. The blended cathode's initial discharge characteristics seem to be an average of the two unblended cathodes at the 4C rate. At this higher rate, unblended $LiMn_2O_4$ performs the best out of the three cathodes. The direct comparison of the discharge characteristics at the 4C rate indicates that the presence of $LiMn_2O_4$ in the blended cathode contributes to improved rate performance compared to unblended $LiCoO_2$. The combined cathode with a 5:5 weight ratio of $LiMn_2O_4$ and $LiCoO_2$ may display a mix of the electrochemical characteristics seen in the unblended cathodes, according to this theory. At low rates, the $LiCoO_2$ component predominates, but the $LiMn_2O_4$ component improves the cathode's rate performance.

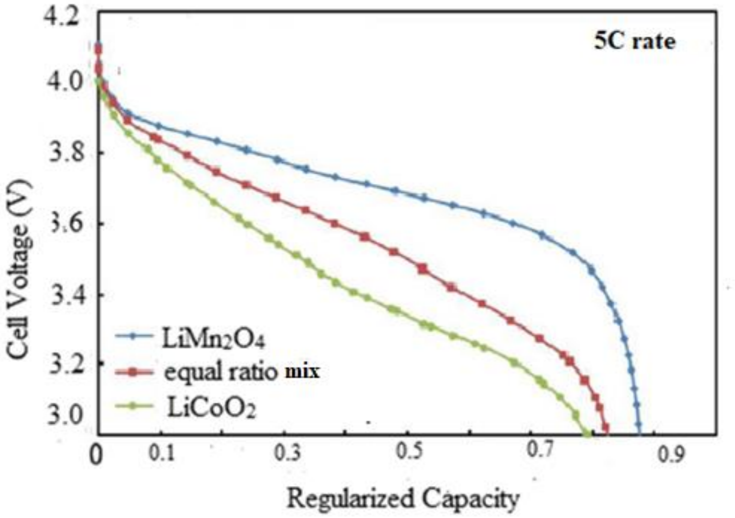

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Figure 3a. Cathode electrode discharge profiles from experimental results consisting unblended $LiMn_2O_4$, $LiCoO_2$ and equal ratio of the mix at 5C rate.

Overall, the results indicate that the blended cathode with the 5:5 weight ratio provides a synergistic effect, where the combination of $LiMn_2O_4$ and $LiCoO_2$ leads to improved electrochemical performance compared to the individual unblended cathodes. This discovery is crucial to comprehending how the cathode material composition affects the Li-ion battery's rate capability and overall performance. High-performance lithium-ion battery design and optimization may be significantly impacted by the blended cathode's enhanced rate performance.

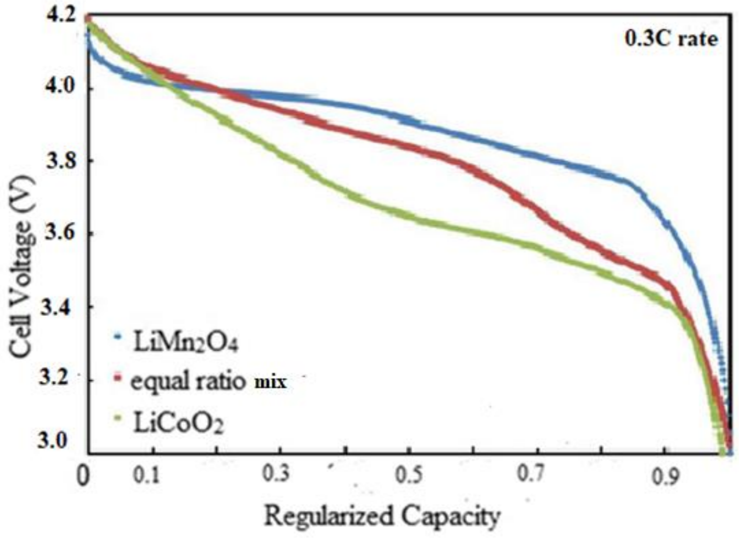

Figure 3b. Cathode electrode discharge profiles from experimental results consisting unblended $LiMn_2O_4$, $LiCoO_2$ and equal ratio of the mix at 0.3C rate.

The unblended $LiMn_2O_4$ cathode's experimental and simulated rate performances are shown in **Figure 4a** of the study at different discharge rates ranging from 0.3C to 4C. The lithium-ion intercalation and de-intercalation reactions take place in two stages, as shown by the two elevations seen in the discharge curve of the $LiMn_2O_4$ spinel cathode. For all discharge rates, the modeling findings are in close agreement with the actual values, especially for the early phases and the lower cut-off voltage of 3.0 V. This agreement between simulation and experiment validates the accuracy of the model in representing the electrochemical behavior of the unblended $LiMn_2O_4$ cathode. In Figure 4b, the experimental and simulated rate performances of the unblended $LiCoO_2$ electrode system are shown at discharge rates from 0.3C to 4C. Comparing Figure 4a and Figure 4b, it can be concluded that the rate capabilities of the unblended $LiMn_2O_4$ cathode are superior to those of unblended $LiCoO_2$. Once again, there is good agreement between the simulated discharge profiles and the experimental results, particularly at the initial stages and cut-off voltage of 3.0 V. At high discharge rates, there is a small variation, but overall, the simulation accurately depicts the main features of the experimental behavior. These results verify that the simulation's model accurately captures the unblended $LiMn_2O_4$ and $LiCoO_2$ cathodes electrochemical behavior, offering important information on their rate capacities and discharge profiles. Indeed, **Figure 4** demonstrates that the regularized discharge capacity is dependent on the discharge rate (C-rate). The discharge curve tends to slope downward with increasing C-rate, suggesting a decline in the cell's total capacity. The main reason for this decrease in capacity is the polarization brought on by the cell's internal resistance. To maximize the design of Li-ion batteries for particular applications and comprehend performance constraints, the model must be able to forecast the rate capabilities and discharge behavior of the unblended cathodes with sufficient accuracy..

The findings show that, especially for the unblended $LiCoO_2$ active material, the capacity difference between various discharge rates is more noticeable in the low output potential difference range. The loss of discharge capacity increases with the discharge rate (c-rate), primarily because of the electrode's contribution from Li-ion diffusion. During discharge, a significant gradient in the concentration of Li-ions is formed within the active material particles when the c-rate is elevated. As a result, the electrode potential drops sharply to the cut-off voltage, which lowers the cell's capacity to discharge energy [12]. The smaller solid-phase Li-ion diffusion coefficient of the unblended $LiCoO_2$ active material, compared to that of the unblended $LiMn_2O_4$ active material (as shown in **Table 1**), supports this observation. The lower Li-ion diffusion coefficient of $LiCoO_2$ implies a slower rate of Li-ion diffusion within the electrode, leading to a larger concentration gradient and more pronounced capacity loss at higher c-rates. This finding emphasizes the significant influence of the discharge rate on the discharge capacity and polarization effects in the studied lithium-ion battery system. The study also presented how crucial it is to take the cathode's contact resistance into account while running simulations. Simulated discharge profiles that initially assumed zero contact resistance in both the positive and negative electrodes differed from the experimental results, especially with regard to the distance between the discharge curves. As seen in **Table 1**, the cathode's contact resistance was raised to a noteworthy value in order to resolve this problem. The computed and experimental findings agreed better with this adjustment, particularly for low c-rates and a cut-off voltage of 3.0 V. To ensure that the simulations match the experimental observations and appropriately represent the electrochemical behavior of the battery system, contact resistance must be taken into account. This allows for a more comprehensive understanding of the battery's performance and behavior, leading to better optimization and design for practical applications.

Table 1. Design variables used to model the battery

Variable design parameters	Graphite	$LiMn_2O_4$	$LiCoO_2$
Diffusion coefficient in solid, m^2s^{-1a}	$3.50x10^{-14}$	$7.90x10^{-14}$	$1.20x10^{-14}$
Reaction rate constant, $m^{2.5}$ $mol^{-0.5}$ s^{-1a}	$1.80x10^{-7}$	$7.50x10^{-7}$	$1.30x10^{-7}$
Residual resistance, Ω m^{2b}	0	0.0019	0.006
Initial SEI resistance, Ω m^{2b}	0.02	0	0
Electrode thickness, μm^c	45	55	55
Volume fraction electrolyte^c	0.4	0.3	0.3
Particle radius, μm^c	10.7	6.7	5.7
Separator thickness, μm^c		25	
Separator porosity, $\%^c$		43	
Initial salt concentration, M^c		1.17	
Tortuosity^d	2.9	3.36	3.36
Conductivity, Sm^{-1d}	100	10	10
Density, g cm^{-3}	2.4	4.4	5.0
Molecular weight, g mol^{-1}	71.59	179.58	106.78

^{a}Estimated parameters, ^{b}Assumed parameters, ^{c}Battery design parameters, ^{d}Reference obtained parameters

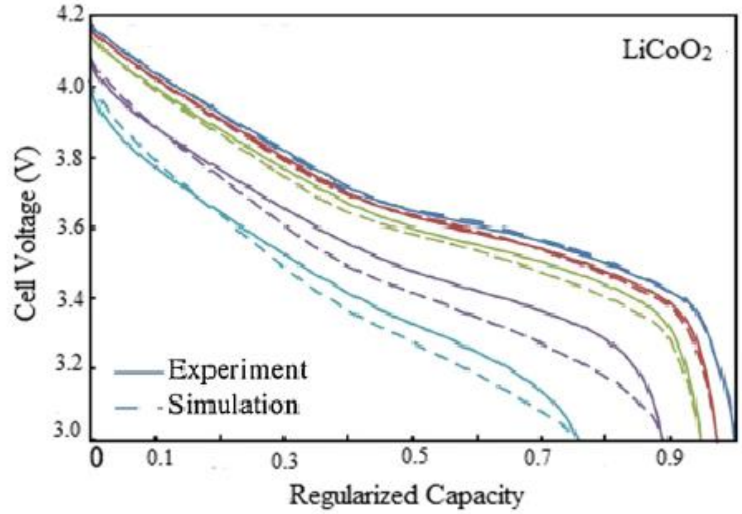

Figure 4a. Cathode formulated $LiCoO_2$ blended experimental and simulation rate performance

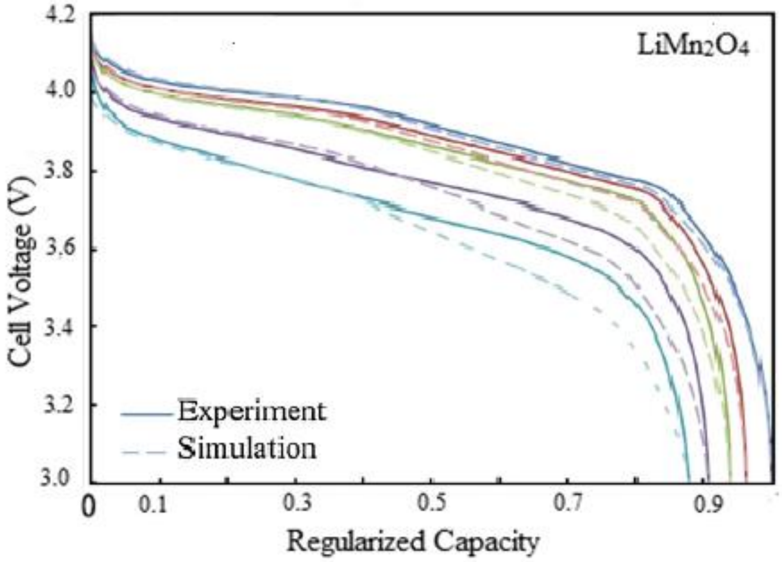

Figure 4b. Cathode formulated $LiMn_2O_4$ blended experimental and simulation rate performance

The experimental and simulated rate performances of the blended cathode with a 5:5 weight ratio of $LiMn_2O_4$ spinel and $LiCoO_2$ are shown in **Figure 5**. The graph unequivocally shows that the blended electrode system's rate performance is much better than the unblended $LiCoO_2$ cathode's. The simulated and experimental data clearly show the blended cathode's better rate performance. The agreement between simulation and experiment is good at low discharge rates, similar to the previous situations, while there may be some differences between the simulated and experimental results at high discharge rates. This indicates that the model, with adjusted contact resistance, accurately captures the behavior of the blended cathode at moderate discharge rates. The slight discrepancies at high discharge rates could be attributed to the complexity of the electrochemical behavior and the limitations of the model at extreme operating conditions.

Overall, the findings highlight the beneficial effect of combining $LiMn_2O_4$ and $LiCoO_2$ in a 5:5 weight ratio. The blended cathode demonstrates enhanced rate performance compared to the unblended $LiCoO_2$ cathode, suggesting a synergistic effect of the two active materials. This improvement in rate performance is essential for applications requiring high power output and rapid charge-discharge cycles. The outcomes further emphasize how important precise modeling and simulation are to comprehending the behavior of intricate battery systems. The simulation results at low and moderate discharge rates agree well with experimental observations when the contact resistance is changed, providing important new information about the blended cathode's electrochemical performance.

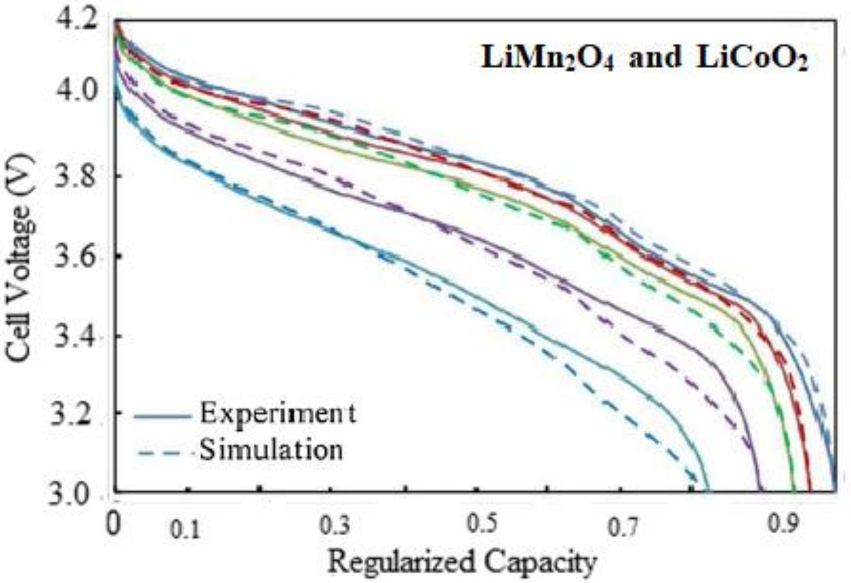

Figure 5. Cathode formulated $LiMn_2O_4$ and $LiCoO_2$ blended experimental and simulation rate performance for 5:5 weight ratio at 0.3C, 0.6C, 1C, 2C and 4C.

Design Analysis

At low discharge rates, the specific energy of the cell containing the unblended $LiCoO_2$ cathode is initially larger than that of the cells having the blended cathode with a 5:5 weight ratio and the unblended $LiMn_2O_4$ cathode, as shown in **Figure 6** of the study. The $LiCoO_2$ cathode's comparatively higher capacitive loading, which permits more energy storage at lower discharge rates, is responsible for this higher specific energy. However, as the discharge rate increases beyond 6C, the specific energy of the cell with the unblended $LiMn_2O_4$ cathode surpasses that of the unblended $LiCoO_2$ system and the alloyed cathode system. The higher usage of the unblended $LiMn_2O_4$ cathode under high-rate conditions, especially at the cut-off voltage of 3.0 V, is responsible for its superior performance at high discharge rates. At these high rates, however, the energy density of the mixed cathode system and the unblended $LiCoO_2$ system is lower. Furthermore, it is observed that at rates below 6C, the energy density of the active material with a 0.5 weight fraction of $LiMn_2O_4$ is lower than the mean value of the energy density of the two unblended active materials ($LiMn_2O_4$ and $LiCoO_2$). However, when the rate exceeds 6C, the energy density of the active material with a 0.5 weight fraction of $LiMn_2O_4$ surpasses the mean value of the energy density of the two unblended active materials. These findings demonstrate how the electrode compositions behave in a rate-dependent manner and how that affects the battery system's specific energy.

The behavior seen in **Figure 6** can be explained by observing varying proportions of current contribution from the two unblended active materials in the blended cathode at varied discharge rates. The active material $LiMn_2O_4$ contributes a larger portion of the current at discharge rates below 6C, while $LiCoO_2$ contributes a larger portion of the current at rates above 6C. The variations seen in Figure 6, where the specific energy of the blended cathode system varies with the discharge rate, are a result of this dynamic behavior, which also affects the cell's specific energy.

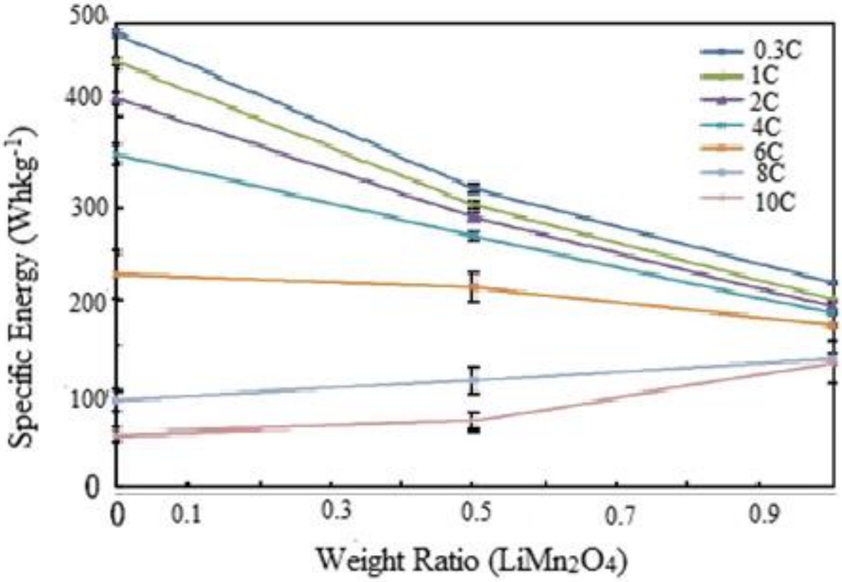

Figure 6. Specific energy versus weight ratio at different discharge rates

These composite electrode materials have the potential to be used in the fabrication of a power-energy hybrid system, as demonstrated by the rate-dependent contributions of each active material in the blended cathode. One active material with comparatively higher power characteristics can control the discharge pulses in a power-energy hybrid system, delivering high-power bursts when required, while another active material with comparatively higher energy characteristics can preserve the system's energy content when the power demand is lower [8]. This characteristic allows for a more balanced usage of the strengths of the active materials, which is beneficial for applications that require both high-power performance and extended runtime.

A useful tool for comparing the impact of various cathode materials when combined to create a composite electrode system is the Ragone plot, shown in **Figure 7**. Plotting specific energy vs specific power is shown here, with both values computed at the lower cut-off voltage of 3.0 V. The plotted results offer valuable insights into the performance of various cathode materials under variable power and energy needs. The specific energy of unblended LiCoO2 is higher at low specific powers, as seen in the Ragone plot, suggesting that it is appropriate for uses requiring longer running times but lower discharge rates. This characteristic is beneficial for devices or systems that need sustained energy delivery over extended periods, such as portable electronics or electric vehicles during daily commuting.

Conversely, unblended $LiMn_2O_4$ exhibits higher specific energy at high specific powers, making it more suitable for applications that demand high power output in shorter durations. This behavior is advantageous for power-hungry devices or systems that require quick bursts of energy, such as power tools or electric vehicles during acceleration and high-speed driving. These results confirm the effects of the cathode materials on the power and energy properties of the composite electrode system and are consistent with the observations shown in **Figure 7**.

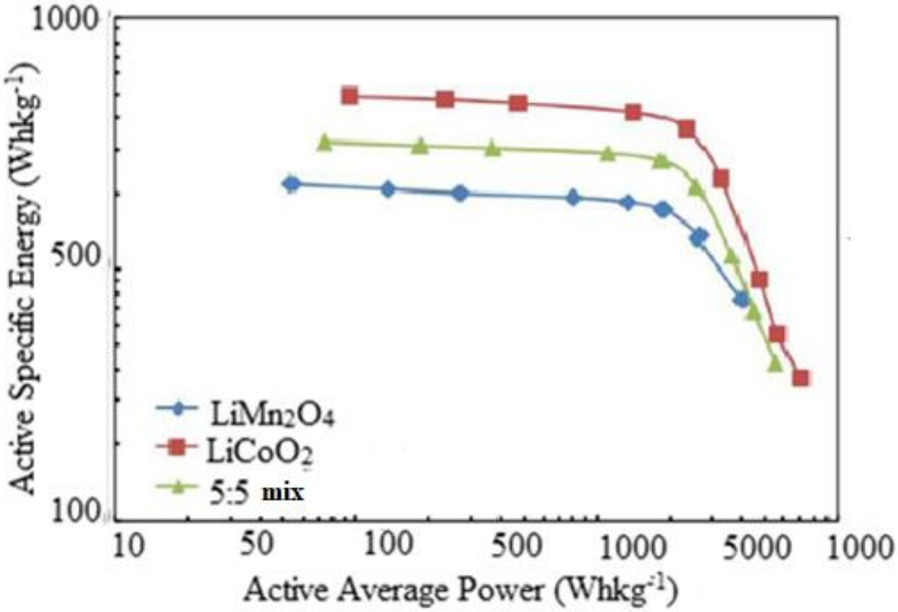

Figure 7. Ragone plot for the various cell compositions

Conclusions

The study conducted in this research aimed to address the limitations of individual cathode or anode active materials in lithium-ion batteries by mixing them together in the positive electrode. Graphite was employed as the negative electrode in the experiment, whereas active materials such as $LiMn_2O_4$ and $LiCoO_2$ made up the positive electrode. The lithium-ion battery model in Multiphysics was used to simulate the cells' galvanostatic discharge characteristics at various rates. Furthermore, the $LiMn_2O_4$ active material's cycle performance was examined, and the single particle model was used to estimate the model's parameters. The experimental results showed that the positive electrode with unblended $LiCoO_2$ active material exhibited high specific energy at low specific powers, indicating its suitability for applications that require longer operating times but lower power outputs. This behavior aligns with the characteristics of $LiCoO_2$, which is known for its higher energy density but relatively lower rate capability. On the other hand, the positive electrode with unblended $LiMn_2O_4$ active material displayed high specific energy at high specific powers, making it more suitable for applications that demand high power outputs in shorter durations. $LiMn_2O_4$ is recognized for its better rate performance but relatively lower energy density compared to $LiCoO_2$.

The combination of the properties of the two active materials in one electrode, a blend of $LiMn_2O_4$ and $LiCoO_2$ displayed above-average electrochemical performance. This finding implies that combining the two materials may result in a synergistic effect whereby the composite electrode gains from each material's advantages while offsetting its disadvantages. The study's overall conclusions demonstrate the possible advantages of combining several active ingredients in lithium-ion battery electrodes. Researchers and engineers may create batteries that combine energy density and power capability, addressing the unique needs of different applications, by carefully selecting and combining the active materials. This approach paves the way for the development of more efficient and versatile lithium-ion batteries with improved overall performance and applicability in a wide range of devices and systems.

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References

[1] A. Yoshino, The Birth of the Lithium-ion Battery, *Angew. Chem. Int. Ed*. Vol.51, no.24, pp.5798-5800, 2012, doi:10.1002/anie.201105006.

[2] Y. Huang, The discovery of cathode materials for lithium-ion batteries from the view of interdisciplinarity. *Interdiscip Mater*, vol.1, no.3, pp. 23-329, 2022, doi:10.1002/idm2.12048.

[3] M. M.Thackeray, Exploiting the spinel structure for Li-ion battery applications: a tribute to John B. Goodenough. *Adv Energy Mater*. vol.11, no.2, doi:10.1002/aenm.202001117.

[4] M. Hosoya, H. Ikuta, T. Uchida and M. Wakihara, The Defect Structure Model in

[5] Nonstoichiometric $LiMn_2O_4$, *Journal of the Electrochemical Society*, vol. 144, no.2, 1997, doi:10.1149/1.1837550.

[6] S. Komaba, K. Hosoya, S. Myung, H. Yashiro, Y.-K. Sun and N. Kumagai, Improvement of cycling performance of $Li_{1.1}$ $Mn_{1.9}O_4$ at 60C by NiO addition for Li-ion secondary batteries, *Electrochimica acta,* vol. 51 pp.5912–5919, 2006, doi:10.1016/j.electacta.2006.03.029.

[7] H. Zheng, J. Li, X. Song, G. Liu and V.S. Battaglia, A comprehensive understanding of electrode thickness effects on the electrochemical performances of Li-ion battery cathodes, *Electrochimica Acta,* vol. 71, no. 1, pp. 258-265, 2012, doi:10.1016/j.electacta.2012.03.161.

[8] K. Hyun-Soo, S.-I. Kim, W.-S. Kim, A study on electrochemical characteristics of

[9] $LiCoO_2/LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ mixed cathode for Li secondary battery, *Electrochimica Acta,* Vol. 52, no. 4, pp. 1457-1461, 2006, doi:10.1016/j.electacta.2006.02.045.

[10] J. Whitacre, K. Zaghib, W. West and B. Ratnakumar, Dual active material composite cathode structures for Li-ion batteries, *Journal of Power Sources,* vol. 177, no. 2, pp. 528–536, 2008, doi:10.1016/j.jpowsour.2007.11.076.

[11] K. Ariyoshi and R. Suzuki, Experimental Measurement and Quantification of the Local Cell Reaction in Blended Lithium Insertion Electrodes, *ChemElectroChem*, vol. 9, no. 10, 2022, doi:10.1002/celc.202200101.

[12] C. Heubner, T. Liebmann, C. Lämmel, M.Schneider and A. Micheal, Synergy Effects in Blended Electrodes for Li-ion Batteries: A Conceptual Clarification, *Batteries & Supercaps,* vol. 5, no. 1, 2022, doi:10.1002/batt.202100171.

[13] A. Paul, J. Christensen and J. Newman, Experiments on and modeling of positive

[14] electrodes with multiple active materials for lithium-ion batteries, *Journal of the Electrochemical Society*, vol. 156, no. 7, 2009, doi:10.1149/1.3129656.

[15] H. Zheng, J. Li, X. Song, G. Liu and V.S. Battaglia, A comprehensive understanding of electrode thickness effects on the electrochemical performances of Li-ion battery cathodes, *Electrochimica Acta,* vol. 71, pp. 258–265, 2012, doi:10.1016/j.electacta.2012.03.161.

[16] F.N. Okonkwo, C.A. Okonkwo and S.C. Nwigbo, Optimization of Lithium-ion Cell Positive Electrode for Maximization of Energy Capacity, *Journal of Engineering and Applied Sciences,* vol. 20, no. 1, pp 643-656, 2022.

[17] Y. Cholipour, future of oil and renewable energy, Department of Engineering N.I.O.C Tehran, Iran, vol. 5, no. 1, pp. 30-37, 2022, doi:10.19184/cerimre.v5i1.31492.

[18] T. Numata, T. Kumeuchi, M. Shirakata, C. Amemiya and M. Yonezawa, Advantages of blending $LiNi_{0.8}Co_{0.2}O_2$ into $Li_{1+x}Mn_{2-x}O_4$ cathodes, *Journal of*

power sources, vol. 97-98, pp. 358-360, 2001, doi:10.1016/S0378-7753(01)00753-4.

[19] N. Imachi, Y. Takano, H. Fujimoto, Y. Kida and S. Fujitani, Layered cathode for improving safety of Li-ion batteries, *Journal of the Electrochemical Society,* vol. 154, no. 5, pp. 412-416, 2007, doi:10.1149/1.2709503.

[20] M.M. Thackeray, E. Lee, B. Shi and J. R. Croy, Review from $LiMn_2O_4$ to partially-disordered Li_2MnNiO_4 the evolution of lithiated-spinel cathodes for Li-ion batteries. *J Electrochem Soc,* vol. 169, no. 2, 2022, doi:10.1149/1945-7111/ac50dd.

[21] S. Künne, J. M. Hesper, T. Lein, K. Voigt, D. Mikhailova, A. Michaelis, M. Winter, T. Placke and C. Heubner, Hybrid High-Voltage $LiNi_{0.5}Mn_{1.5}O_4$/Graphite Cathodes Enabling Rechargeable Batteries with Simultaneous Anion- and Cation Storage, *Batteries & Supercaps*, vol. 6, no. 9, 2023, doi:10.1002/batt.202300284.