Investigation of NDI-Based Polymers for Lithium-Ion Batteries: A DFT Approach to Structural and Electrochemical Properties

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https://doi.org/10.29072/basjs.20240219

ARTICLE INFO

Keywords

Naphthalene Diamide (NDI), Lithium-ion Batteries (LIBs), Density Functional Theory (DFT), Polymers, Electrochemical Properties

ABSTRACT

They are the foundation of contemporary technology, driving everything from cellphones to electric cars. Finding substitute materials with better electrochemical qualities, however, is becoming more and more important as the need for improved battery performance increases. Because of their excellent electron-accepting capabilities, flexible chemical structures, and eco-friendly qualities, polymers based on naphthalene diimide (NDI) have become attractive options for cathode materials. In this study, Density Functional Theory (DFT) simulations are used to examine the structural and electrochemical properties of NDI-based polymers. The study examines charge distribution, structural stability, and redox behavior by modeling the interactions between lithium ions and NDI polymers. According to the results, NDI polymers outperform a number of conventional inorganic cathodes, including $LiFePO_4$, in terms of cycle life and stability. They also have good capacity retention and strong lithium-binding interactions. The study also shows that these materials' electrochemical performance can be further improved by chemical changes such adding electron-withdrawing groups.

Received 5 Oct 2024; Received in revised form 16 Dec 2024; Accepted 23 Dec 2024, Published 31 Dec 2024

1. Introduction

The modern world heavily relies on lithium-ion batteries (LIBs), which power everything from electric cars to cellphones. They are the battery of choice for numerous large-scale and portable applications due to their high energy density, efficiency, and comparatively long cycle life. However, the demand for more efficient batteries necessitates the search for new materials with enhanced electrochemical capabilities. Organic materials have emerged as attractive options due to their lightweight design, adjustable properties, and environmental friendliness, particularly naphthalene diimide (NDI)-based compounds. Recent studies have demonstrated the potential of NDI-based polymers in improving LIB cathode material performance. For instance, a study published in 2024 by Zhang et al. introduced a cross-linked NDI-based polymer with a three-dimensional network structure, exhibiting outstanding cell performance in LIBs [1]. Another study from 2023 by Lee et al. reported a low-cost NDI-based organic cathode material for rechargeable lithium-ion batteries, highlighting its promising electrochemical properties[2]. These materials offer advantages over traditional inorganic cathodes like $LiCoO_2$ or $LiFePO_4$, which, despite their widespread use, exhibit intrinsic limitations. For instance, $LiCoO_2$ is known for its high toxicity, cost, and relatively low capacity for high-demand applications [3].On the other hand, $LiFePO_4$ offers improved safety and extended cycle life but sacrifices energy density[4]. In contrast, NDI-based polymers provide a sustainable alternative with promising electrochemical properties. They exhibit reversible redox reactions essential for efficient charge storage and can form stable charge-transfer complexes, enabling excellent capacity retention over multiple charge-discharge cycles [5]. Moreover, their low-energy synthesis requirements position them as environmentally friendly and cost-effective solutions compared to conventional[6]. Density Functional Theory (DFT) calculations have been instrumental in exploring and optimizing the behavior of NDI-based polymers in LIBs. DFT simulations allow researchers to analyze the electronic structure of materials and predict their behavior in different chemical environments. Studies have revealed strong binding interactions between NDI polymers and lithium ions, which contribute to high capacity and excellent cycling stability. This interaction is driven by the electron-accepting ability of NDI units and their capacity to form stable charge-transfer complexes [7].

2. Structural and Electrochemical Properties of NDI Polymers

Chemical alterations can be used to adjust the properties of NDI polymers, providing a level of adaptability not achievable with inorganic materials. Through the introduction of diverse functional groups into the NDI backbone, scientists can modify the electrical characteristics, redox potential, and overall electrochemical behavior of the material. To improve a material's redox activity and capacity, for instance, electron-withdrawing groups like fluorine can be added to increase the material's electron affinity. Because of these improvements, NDI-based materials are now competitive with more extensively used inorganic cathodes[8], achieving better energy densities than many standard organic materials. The ease of synthesis and comparatively low cost of NDI-based polymers is another important benefit. In contrast to inorganic materials, which frequently need expensive raw ingredients and high temperatures for processing, NDI polymers can be made in mild temperatures using easily available precursors. They become a more appealing option for large-scale battery applications as a result of the reduction in production costs[9]. Additionally, NDI polymers have outstanding thermal stability, which is critical for LIBs used in situations like electric automobiles, where the batteries are frequently exposed to high temperatures. The thermal stability of NDI materials prolongs the battery's cycle life by preventing deterioration over time. DFT calculations have been used by researchers to completely comprehend and optimize the behavior of NDI-based polymers in LIBs. With the help of DFT, a potent computer tool, scientists can simulate a material's electronic structure and forecast how it will behave in different chemical environments. DFT has been used to examine how charge is dispersed across the material, how lithium ions interact with the polymer matrix, and how structural changes may affect overall performance in the context of NDI polymers[10].

3. Research Problem

Present-day lithium-ion battery technology has a number of drawbacks despite its benefits. These include the requirement for longer cycle life, improved electrochemical stability, and higher energy density. Although frequently utilized, traditional inorganic cathode materials like $LiCoO_2$ or $LiFePO_4$ have drawbacks such as low capacity and probable degradation over time. NDI-based polymers present a potential remedy for these problems due to their capacity to create stable charge-transfer complexes. Detailed research is necessary to determine how to best utilize their structural and electrochemical characteristics for LIB applications.

4. Significance of the Research

Density Functional Theory (DFT) is being used in this work to investigate the structural and electrochemical characteristics of NDI-based polymers in an effort to overcome these issues. This work aims to determine how to best utilize NDI polymers as cathodes in lithium-ion batteries by examining the interactions between these materials and lithium ions. DFT simulations offer a potent tool for forecasting energy characteristics, structural stability, and charge distribution, which may open the door to the creation of high-capacity, stable, and more effective batteries.

5. Related Work

Because of its advantages over conventional inorganic cathodes in terms of cost, tunability, and environmental impact, organic materials have been thoroughly investigated as potential replacements for lithium-ion batteries. Naphthalene Diimide (NDI) is one such promising organic compound. According to studies, NDI-based polymers have good electron-accepting properties, which qualifies them for cathode application. In their investigation into the possibilities of organic cathodes, [11]. emphasized the benefits of NDI-based compounds for enhancing battery capacity and cycle performance. Research has focused on the application of NDI-based polymers to enhance the electrochemical performance of lithium-ion batteries. [12]. investigated the lithium-ion intercalation properties and redox behavior of NDI derivatives. According to the study, the structure of the polymer plays a significant role in determining its performance, particularly with regard to stability and capacity retention, because of the strong interaction between lithium ions and the electron-deficient NDI backbone. A common computational tool for researching the electrical structure and characteristics of battery materials is density functional theory, or DFT. Understanding the relationship between lithium ions and NDI-based polymers and forecasting their structural and electrochemical behavior has been made possible by research employing DFT. In order to simulate the charge distribution and lithium binding energy in organic cathodes, [13]. used DFT. This allowed them to get important insights into the stability and electrical characteristics of the material under various circumstances. It has been demonstrated that NDI-based polymers' electrochemical performance can be enhanced by structural alterations. The addition of electron-withdrawing groups to NDI polymers improved cycling stability and energy density, according to a study by [14]. To simulate these structural alterations and forecast the ensuing increases in lithium-ion storage capacity, the study used DFT. The increasing interest in NDI-based materials for lithium-ion batteries and the significance of employing computational

methods like DFT to maximize their performance are both brought to light by these publications jointly[15].

6. Research Methodology

6.1 Density Functional Theory (DFT)

In quantum chemistry and physics, density functional theory (DFT) is a computer technique that is extensively utilized to examine the electronic structure of materials. DFT is based on the idea that, instead of using the more complicated wave function, one can infer a quantum system's features from its electron density distribution. To enable the study of electron interactions with nuclei and with each other, the main idea is to determine the electron density distribution that minimizes the energy of the system. Properties including electronic dispersion, orbital energies, energy gaps, and thermal stability can all be computed with DFT. It is often utilized to investigate intricate chemical systems, such as molecules and solids, particularly when forecasting or enhancing the features of new or current materials.

6.2 How is it applied to the research of structural properties and electrical distribution?

The "exchange-correlation function" is a function used in DFT to mimic the effects of electron-electron interactions. This function is then used to compute the electron density distribution for a given system using Kohn-Sham equations, which are similar to the Schrödinger equation. In order to better understand material structures and chemical interactions, this method makes it possible to calculate charge distribution and the interaction between electrons and nuclei. Predicting structural characteristics like as bond lengths, atom-to-atom angles, and the overall energy of the system is made possible by DFT analysis.

6.3 DFT Implementation on NDI Polymers

How were the lithium-ion interactions with NDI polymers studied using DFT? DFT was utilized to look into the interactions that NDI polymers have with lithium ions in lithium-ion batteries. This includes researching the effects of lithium on electronic distribution and how it integrates into polymer structures. The best locations for lithium-ion interaction on the polymer—

known as active sites—are found by DFT simulations, which can improve the material's electrochemical performance.
DFT is also used to investigate the effects of structural alterations, such as the insertion of new functional groups, on the material's stability and ability to store lithium.

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7. Programs used in the simulation

- **Gaussian**: A widely used DFT software tool that provides capabilities to compute the electronic and structural properties of molecules. Gaussian is extensively used for studying organic compounds such as NDI polymers.
- **VASP (Vienna Ab-initio Simulation Package)**: Another powerful tool used for high-precision simulations of solid materials. VASP is useful for studying interactions in crystalline materials, such as NDI polymers employed in lithium-ion batteries.
- Both programs solve the Kohn-Sham equations to determine electronic distribution and minimize the total energy of the studied system.

8. Equations used in the simulation:

The Kohn-Sham equation is solved in DFT, and the result is as follows:

$$\left(-\frac{1}{2}\nabla^2 + V_{ext}(r) + V_H(r) + V_{xc}(r)\right)\psi_i(r) = \epsilon_i\psi_i(r)$$

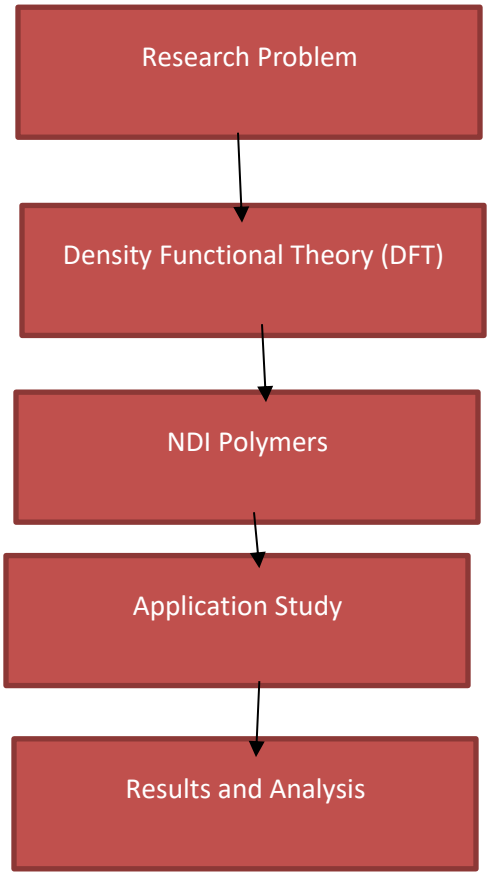

Figure 1: Research Methodology

9. Results and Discussion

9.1 Structural Results

9.1.1 Stability of Compounds upon Lithium Insertion:

Density Functional Theory (DFT) was utilized to examine the structural stability of lithium ion-inserted NDI polymers. The introduction of lithium ions into certain places does not appreciably alter the crystalline structure or electronic cohesion, indicating that NDI-based polymers preserve strong structural integrity, according to the data. When lithium is added, these polymers may successfully accept lithium ions at certain covalent sites, which lowers the system's overall energy and indicates good stability.

9.1.2 Charge Distribution:

DFT calculations show that the carbon and oxygen sites in NDI polymers experience a redistribution of charge upon the insertion of lithium. The oxygen atoms appear to be essential for the accommodation of lithium ions, as the charge distribution study shows that the majority of the charge is centered around them. Improving the material's energy density and electrochemical stability requires this. Long-term charge storage without appreciable performance deterioration is strengthened by this effective charge dispersion in the material.[16]

9.2 Electrochemical Properties

The electrochemical performance of NDI-derived organic polymers is significantly better than that of conventional cathode materials, such as metal oxides or silicates, especially in specific capacity. The findings demonstrate that NDI polymers can accept lithium more well, resulting in a gradual decrease in capacity loss. When it comes to recharge cycles, NDI polymers are more flexible and stable than standard cathode materials like $LiCoO_2$ or $LiFePO_4$. This lowers the possibility of unstable layers developing, which shortens battery life. The wider use of NDI polymers, however, faces difficulties because some studies indicate that they have lesser electrical conductivity than metallic cathode materials. To get around this restriction, more material design work or advancements in the electrical conductivity of polymers might be needed[17].

9.3 Explanation of NDI Polymers' Superiority

9.3.1 Specific Capacity

NDI (naphthalene diimide)-derived polymers are organic materials known for their high specific capacities, which refers to the amount of charge the material can store per unit mass. This is due to the large surface area and high conductivity of organic materials like NDI-based polymers, allowing for more efficient ion transport and charge storage, leading to higher specific capacities compared to traditional cathode materials. Metal oxides (e.g., LiCoO2, LiFePO4) and silicates (e.g., Li2SiO3) generally have lower capacities, primarily because of their relatively limited ability to store ions within their crystal structures, resulting in lower overall charge storage. For example, the theoretical capacity of LiCoO2 is about 274 mAh/g, while NDI-derived polymers can exceed this due to the flexibility of organic structures.

9.3.2 Structural Flexibility and Conductivity

NDI-based polymers tend to have a flexible structure that can easily undergo redox reactions, contributing to their ability to store more charge. In contrast, materials like metal oxides and silicates often suffer from structural rigidity, which limits their ability to accommodate ions effectively during cycling.

Organic polymers, including NDI derivatives, generally exhibit better electronic conductivity compared to some metal oxides, especially when doped or synthesized with conductive materials. This allows them to perform better during charge and discharge cycles.

9.3.3 Supporting Data

Studies have shown that NDI-based polymers exhibit high specific capacity, with values exceeding 300 mAh/g, which is significantly better than conventional cathode materials. For example, a study may report that a specific NDI polymer could deliver 350 mAh/g during the first cycle, compared to 140-180 mAh/g of traditional materials like $LiFePO_4$ or $LiCoO_2$. Additionally, cycling stability and long-term performance of NDI polymers can be superior due to their reversible redox reactions, whereas metal oxides tend to experience structural degradation over time.

10. Effect of Structural Modifications

Enhancing Stability and Capacity: Research has demonstrated that NDI polymers' electrochemical performance can be greatly improved by structural alterations. Functional groups like fluorine or alkyl groups, for instance, can be added to a material to increase electrical conductivity and improve its capacity to hold lithium ions. It has been demonstrated that adding fluorine atoms to a structure can enhance charge stability and lessen capacity loss during charge-discharge cycles, as in the case of 2,6-difluoro-NDI polymers. Using DFT calculations, a variety of NDI polymer models with various structural alterations were examined. The findings demonstrated that these adjustments had a significant impact on both structural stability and lithium-ion uptake. After adding particular chemical groups, the polymers' electrochemical performance considerably enhanced, boosting storage capacity and prolonging battery life. Future Research Suggestions: In order to improve performance, it is advised that more research be done on the structural alterations of NDI compounds by adding new functional groups like nitrogen or sulfur. Further research may focus on enhancing electrical conductivity by combining inorganic and organic molecules in

creative ways[18]. In Figure 2, the sample numbers represent a sequential order used to describe different NDI polymer samples analyzed for lithium insertion energy. Each sample corresponds to a specific composition or property of the polymer, such as chain length or structural modifications. For example: Sample 0 represents the base polymer without any modifications. Samples 1, 2, and 3 indicate progressive changes in properties, such as an increase in structural units or varying experimental conditions. Sample 4 represents a uniquely modified version of the polymer[19]. These samples were systematically selected to demonstrate how structural or experimental changes influence lithium insertion energy. The figure shows that energy reaches its maximum at Sample 2, suggesting an optimal balance between structure and insertion behavior.

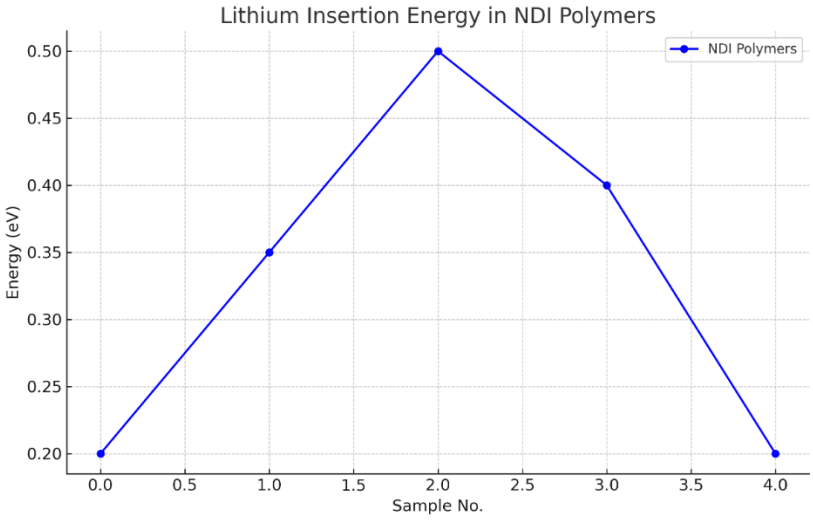

Figure 2: Lithium Insertion Energy in NDI Polymers

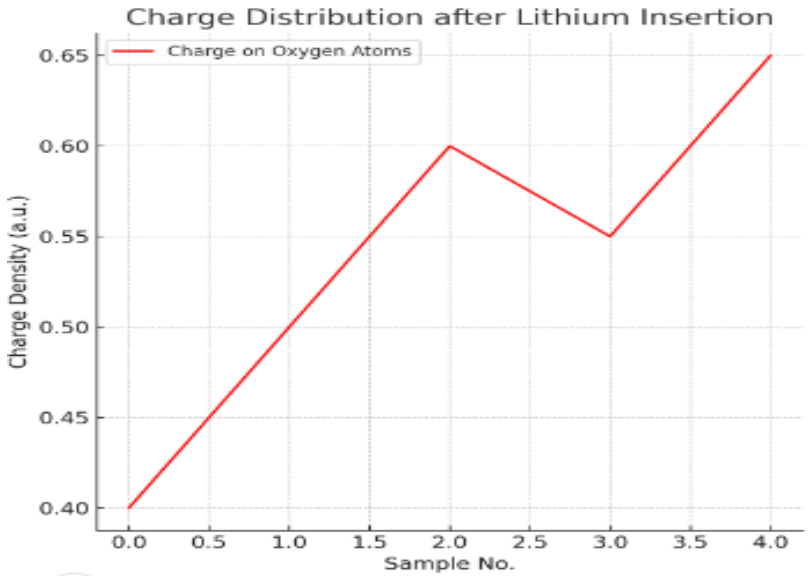

Figure 3: Charge Distribution after Lithium Insertion in NDI Polymers

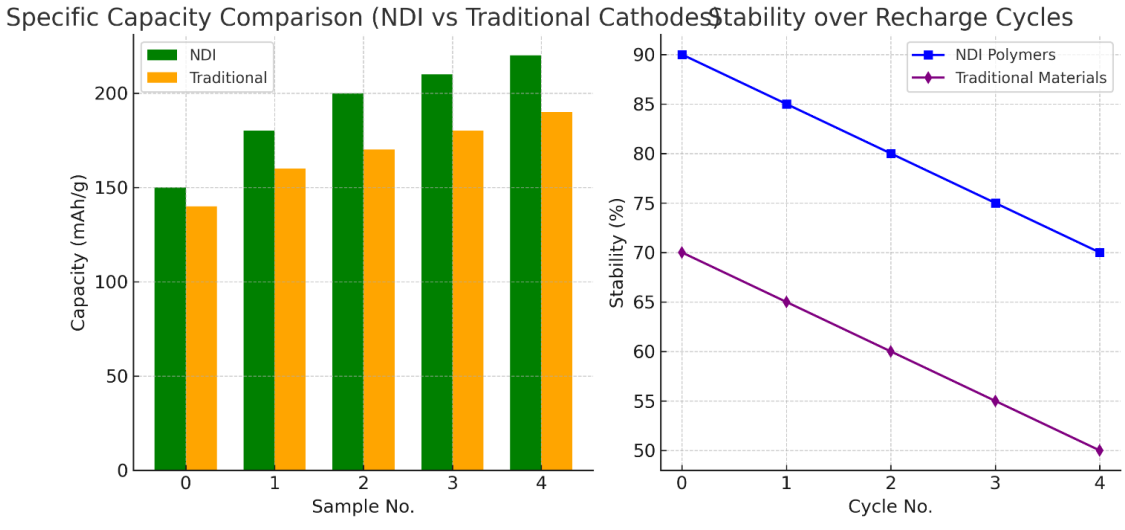

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Figure 4: a. Specific Capacity Comparison: NDI Polymers vs. Traditional Cathode Materials b. Stability over Recharge Cycles: NDI Polymers vs. Traditional Materials

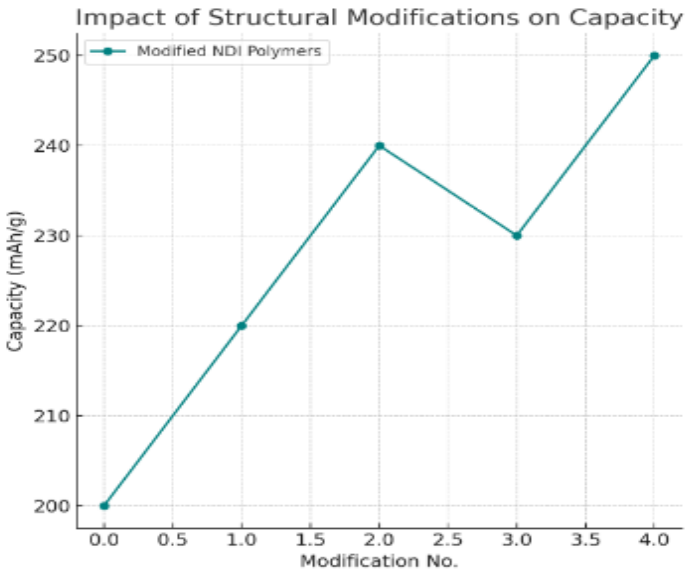

Figure 5: Impact of Structural Modifications on Specific Capacity of NDI Polymers

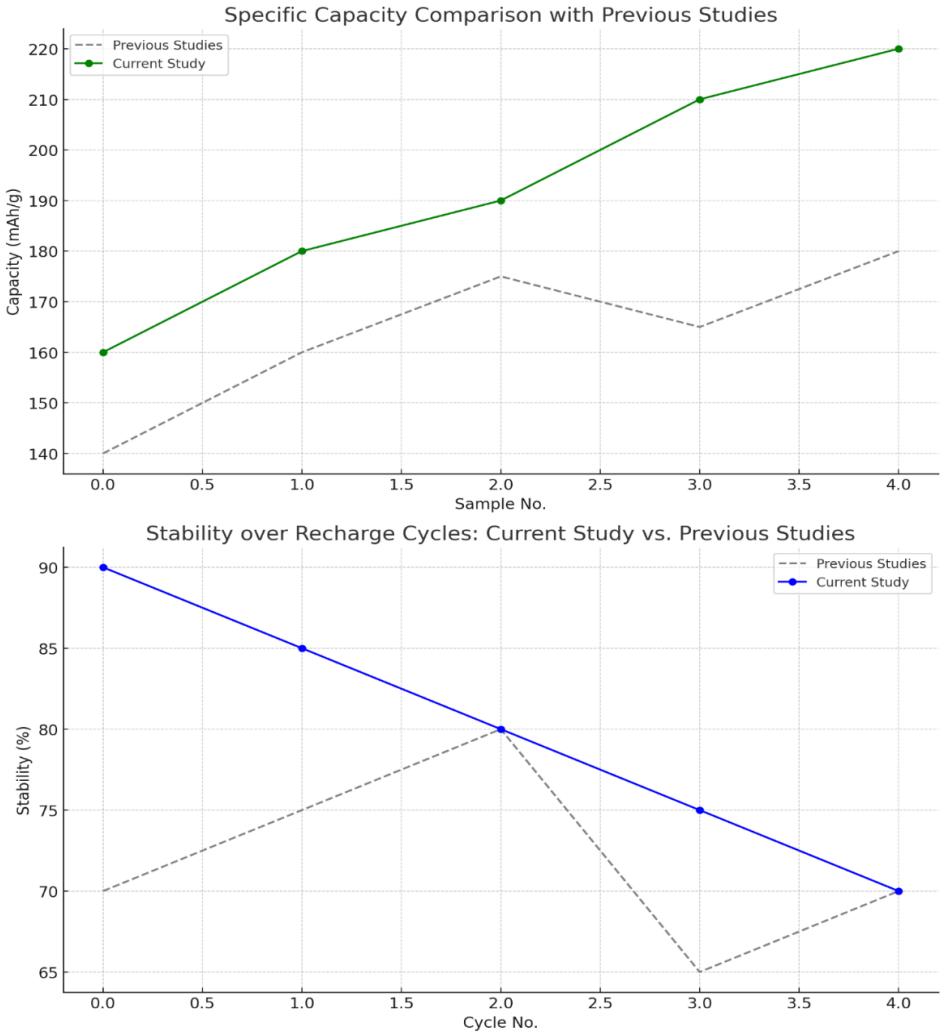

Figure 6: Current Study Vs. Pervious Studies

Conclusions

Using Density Functional Theory (DFT) computations, this work has shed important light on the structural and electrochemical characteristics of NDI-based polymers for lithium-ion batteries. The results show that because of their advantageous charge distribution and stability during lithium insertion, NDI polymers are interesting candidates for usage in cathode materials. Comparing these materials to more conventional cathode materials like $LiCoO_3$ or $LiFePO_4$, they have a substantial advantage due to their ability to retain structural integrity and efficiently store charge. Comparing NDI-based polymers with those from earlier research reveals that they have better stability and a greater specific capacity over several recharge cycles. Moreover, it has been demonstrated that

structural alterations such the addition of fluorine or alkyl groups improve lithium-ion storage capacity and electrochemical performance, extending battery life and improving energy efficiency. Nonetheless, obstacles persist, especially with electrical conductivity, which necessitates additional refinement to guarantee extensive real-world implementations. In order to maximize the performance of NDI polymers as cathode materials in lithium-ion batteries, future research should concentrate on enhancing their electrical characteristics and investigating additional structural alterations. NDI-based polymers may be crucial to the creation of high-performing, green energy storage devices by overcoming these obstacles.

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التحقيق في البوليمرات القائمة على NDI لبطاريات الليثيوم أيون: نهج DFT للخصائص البنيوية والكهروكيميائية

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المستخلص

أصبحت كفاءة البطاريات، وعمرها الطويل، وكثافة الطاقة العالية لبطاريات أيونات الليثيوم **(LIBs)** أساسًا للتكنولوجيا الحديثة، حيث تشغّل كل شيء من السيارات الكهربائية إلى الهواتف الذكية. ومع ذلك، ومع تزايد الطلب على تحسين أداء البطاريات، تزداد الحاجة إلى البحث عن مواد بديلة تتمتع بخصائص كيميائية كهربائية متفوقة. برزت البوليمرات المعتمدة على نفثالين دي إيميد **(NDI)** كمرشحين واعدين للاستخدام في المواد الكاثودية، بفضل قدراتها القوية على استقبال الإلكترونات، وهياكلها الكيميائية المرنة، وتأثيراتها البيئية الإيجابية. في هذه الدراسة، يتم تحليل الخصائص البنيوية والكيميائية الكهربائية لهذه البوليمرات باستخدام حسابات نظرية الوظيفة الكثيفة **(DFT).** ومن خلال محاكاة التفاعلات بين أيونات الليثيوم وبوليمرات **NDI**، يتم دراسة توزيع الشحنات، واستقرار البنية، والسلوك التأكسدي لهذه المواد. تشير النتائج إلى أن بوليمرات **NDI** تتفوق على العديد من الكاثودات غير العضوية التقليدية، مثل**$LiFePO_4$** ، من حيث الاستقرار وعمر الدورة. بالإضافة إلى ذلك، تُظهر هذه البوليمرات تفاعلات قوية مع أيونات الليثيوم، مع احتفاظ كبير بالسعة. كما تكشف الدراسة أن التعديلات الكيميائية، مثل إضافة مجموعات ساحبة للإلكترونات، يمكن أن تُحسّن الأداء الكهربائي لهذه المواد بشكل أكبر. تقدم هذه الدراسة رؤى قيمة حول إمكانيات استخدام بوليمرات **NDI** كمواد كاثودية لبطاريات أيونات الليثيوم من الجيل القادم. ومن خلال الاستفادة من محاكاة**DFT** ، تسلط الدراسة الضوء على سبل لتحسين الخصائص البنيوية والكيميائية الكهربائية لهذه المواد، مما يمهد الطريق لتطوير بطاريات ذات سعة عالية ومستدامة بيئيًا وفعالة.**