

Intercalation reaction in lithium-ion battery: effect on cell characteristics

Theodore Azemtsop Manfo¹ and Mustafa Ergin Şahin¹

¹Recep Tayyip Erdogan University, Faculty of Engineering and Architecture, Department of Electrical and Electronics Engineering, Rize, Türkiye

Article Info

Article history:

Received 08.12.2023

Revised: 27.12.2023

Accepted: 30.12.2023

Published Online: 31.12.2023

Keywords:

Lithium-ion battery

Electrolyte

Intercalation

Graphite

Voltage

Energy efficiency

Abstract

Lithium-ion batteries (LIBs) are vital components in mobile devices and electric vehicles (EVs) due to their high energy density and long lifespan. However, to meet the rising demand for electrical devices, LIB energy density must be improved further. Anode materials, as a key component of lithium batteries, significantly improve overall energy density. LIBs are a widely utilized electrochemical power source in EVs and energy storage. LIBs have proven to be consistent because of their superior power density, which is directly related to the type of cathode, and extended lifespan in comparison to other types of rechargeable batteries. LIBs are developed with suitable electrolytes through a complex pathway that almost parallels advances in electrode chemistry. This work concentrates on the intercalation of alkali metal ions (Li^+) into graphite, summarizing the important advances from experiments and theoretical calculations that underlie the close host-guest relationships and their underlying mechanics. This study elucidates the effect of the intercalation mechanism on the electrode surface to achieve high-performance LIBs. Lithium metal ions in graphite are intercalated into monovalent and multivalent ions in layered electrode materials. This will result in a better understanding of intercalation chemistry in host materials for storage and conversion applications. This review emphasizes the impact of lithium intercalation chemistry on the battery cell using different types of electrode materials to improve its performance. It also studies the influence of the electrode properties on the LIB technology.

1. Introduction

Energy is a key component of any society's progress. It is also needed in industrial settings. As a result, the key concern is to increase the efficiency with which this energy is produced, stored, and delivered [1]. The rapid growth of Li-ion battery technology has piqued the interest of academics [2]. LIBs are currently the market's principal energy source and are widely used in a range of industries, namely gadgets, car batteries, and renewable energy systems [3]. LIB energy density can usually be increased by using high-voltage active cathode materials, anode materials, and electrodes [4,5].

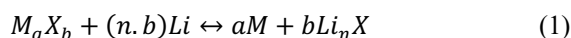
In 1976, Whittingham conducted a significant study published in science [6-8], demonstrating that TiS_2 is an effective host for Li^+ intercalation for energy storage. Recent publications have provided insights into the fundamental characteristics of Li, TiS , and other intercalation compounds. The limitations of traditional energy storage systems such as batteries are their slow charging and short life span limitations [9]. Due to the aggressive reaction of alkali metals with water, LIBs used flammable organic Li^+ electrolytes [10]. Current LIB designs typically feature a carbon (graphite) anode and a transition metal oxide intercalation host as a cathode [11]. Many countries have simultaneously studied the reversible incorporation of Li^+ into graphitic carbon. This work demonstrated that Li^+ is reversibly incorporated into graphitic carbon to form LiC_6 [12]. The wireless revolution started with the introduction of battery-powered mobile phones, made possible by advancements in technology [13]. LIBs are found in hybrid and electric automobiles, but they have shortcomings and efforts are underway to replace them [14]. Goodenough recently

released a perspective article called "Outlook on Lithium-ion Battery" in Science China Chemical [15], which discusses the past, and present challenges, and potential research paths for the widely used energy storage technology.

The LIB has undergone continuous improvements in intercalation materials over its nearly twenty-year lifespan, and LiCoO_2 replacements like $\text{LiNi}_{1-y-z}\text{Mn}_y\text{Co}_z\text{O}_2$, LiFePO_2 , and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ have been introduced at different rates, leading to gradual performance enhancements. However, all of these materials have inherent capacity constraints due to their redox operation and structural characteristics. Many years have elapsed since the discovery of high-capacity electrode materials that can be formed by electrochemistry with lithium in metals and semi-metals. These alloying reactions yield exceptionally large capacities in both weight and volume (examples include silicon with 8365 mAh cm^{-3} and 3590 mAh g^{-1} , graphite with 975 mAh cm^{-3} and 372 mAh g^{-1}). " However, the dealloying process introduces enormous volume changes that cause substantial stresses in the active material particles and generally also in a composite electrode, which complicates their practical application. When cycling these modifications occur, de-cohesion increases, particle displacement occurs and capacity is lost [16,17]. New approaches to avoid such problems have been studied [18], but ones that limit the effects of volume changes include the change in the active material composition, conductive additive, and polymeric binder in the formulation of electrodes; this, however, reduces the overall capacities of all components used in any electrode assembly. However, efforts in this direction were quite successful, and batteries with

composite negative electrodes made from tin (Sn) became commercially viable [19].

The entry of the twenty-first century started attracted by a modern reactivity concept: the reversible electrochemical response of lithium with moving metal oxides [20], which can be generalized as follows equation (1):



Where, M is a transition metal, X is an anion, and n is the formal oxidation state of X .

Conversion processes for various oxides and sulfurs had previously been documented [21,22], with varying degrees of reversibility discovered. Because of the difficulty in intercalating lithium, numerous transition metal complexes with no vacant sites in the structure were ignored. The nanometric nature of the metal particles has been demonstrated to be preserved even after numerous reduction-oxidation cycles [23].

As the largest and fastest-growing battery chemistry on the market [24], higher voltage and capacity materials, as well as a more efficient cell structure, increase energy density. The use of mechanically, thermally, and electrochemically durable components, in conjunction with a battery management system, assures a long service life. It is a challenging task for the battery community to optimize all variables at the same time without compromising safety [25]. This review tends to provide a deep explanation of the influence of the intercalation and correlation between the electrode materials and electrolytes in rechargeable LIBs.

Despite enormous effort and money in boosting Research and Development [26], the majority of battery advancement has occurred at the production level rather than owing to material breakthroughs. There is a deep experimental understanding of how to increase performance and economics, but there are numerous fundamental mysteries about what happens in batteries.

Rechargeable batteries, as the oldest technology for electrical energy storage (EES), are widely employed in everyday life and industrial applications [27]. LIBs are also increasingly being used in applications such as EVs and hybrid electric cars (HEVs), the military, and the aerospace industry [28, 29, 30]. LIBs are the most widely used electrical energy storage technology for a wide range of commercial applications today [31]. This work aims to emphasize the comparison of the properties of some suitable electrode materials used for rechargeable LIBs based on intercalation reactions and their effect on battery performance.

2. Background

Whittingham [32] created the first Li-intercalation cathode in 1972 using titanium disulfide (TiS_2) to increase its voltage potential. This was within the stable potential range of ether below 3.0 V. However, the ester is unstable above 4.0V. Whittingham built a high-energy battery with a titanium disulfide positive electrode and a lithium metal negative electrode in 1976. Figure 1 shows a LIB created by M. Stanley Whittingham [9].

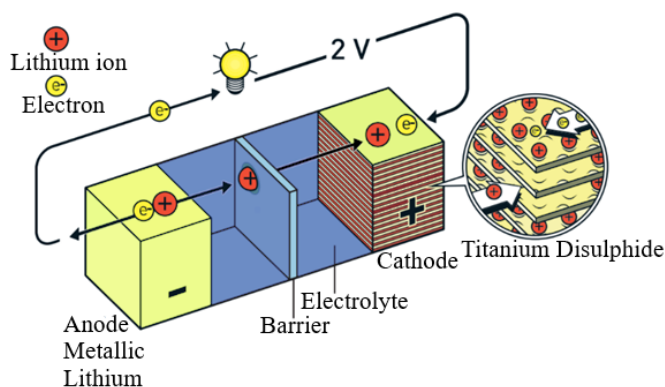


Figure 1. The first lithium-based rechargeable [9]

Whittingham's strategy, on the other hand, was insecure. After Goodenough found metal oxides (such as lithium cobalt oxide, $LiCoO_2$) as high-potential cathode materials, replacing esters with ethers was unavoidable [33]. John Goodenough and Akira Yoshino refined the technology by substituting the cathode and anode with lithium cobalt oxide and graphite, respectively. Stanley Whittingham invented the first functioning lithium battery in the early 1970s, taking advantage of lithium's immense driving energy to release external electrons [9]. Yoshino of Asahi Kasei Corporation invented the first $Li_{1-x}CoO_2/C$ cell, which Sony Corporation marketed as a mobile phone and a camcorder [26]. Since then, the amount of energy stored in a handheld LIB has been effectively increased to more than 3.0 Ah in the 18 650 cells that are already accessible [34].

In the early 1950s [35], ethylene carbonate (EC) and propylene carbonate (PC) were the two most prominent members of the well-known nonaqueous solvent, caustic carboxylic ester, or carbonate-containing ester family. Akira Yoshino was able to broaden the concept of intercalation by studying diverse carbonaceous materials. Secondary batteries constructed from this unique mix provide consistent charging and discharging over a large number of cycles over a lengthy period [36].

$LiCoO_2$ has been improved by adding components that stabilize the crystal shape and enhance capacity. A comparative analysis of Figure 2 shows the significant contribution of Goodenough and others who made to the chemical tinkering of various cathode components. These include $LiCo_{1-x}Ni_xO_2$, $LiMnO_2$, and olivine-based $LiFePO_4$.

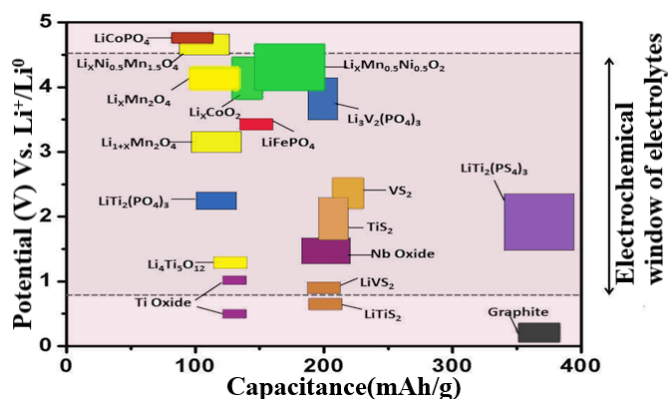


Figure 2. Voltage vs. capacity of various cathode materials about the organic electrolyte window (e.g. 1M $LiPF_6$ in organic carbonate).

The non-aqueous electrolyte propylene carbonate allows for high voltage operation (3.6V), graphite solves the safety concerns linked with lithium steel anodes, and LiCoO₂ makes the material robust and strong enough for manufacturing and long-term cycling became. The secondary LIB typically operates at 3.7 V and has a capacity of 150 mAh g⁻¹. Intercalation and de-intercalation of lithium electrochemically in graphite were successfully shown in the first experiment ever carried out by Rachid Yazami in 1982 [37,38]. Figure 3 shows the intercalation process of Li⁺. Lithium ions will enter the graphite layer and mix with carbon atoms during the charging process. This necessitates that the anode material generates an exceptionally high voltage.

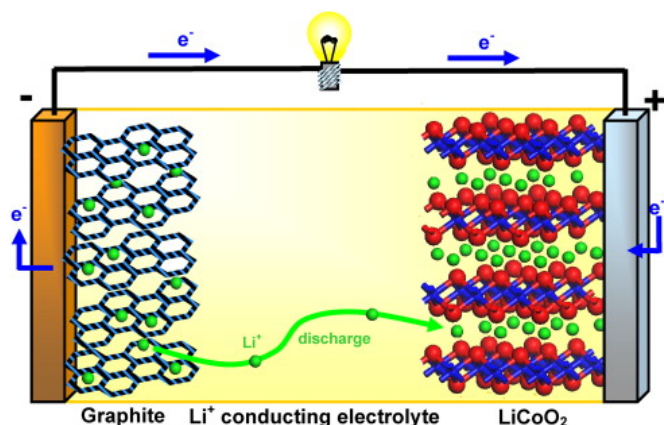


Figure 3. A lithium-ion battery diagram, with the non-aqueous liquid electrolyte LiPF₆ ethylene carbonate/dimethyl carbonate as the electrolyte that separates the negative electrode and graphite, from the positive electrode, LiCoO₂ [39]

As a result, several electrode materials have been investigated to prevent the negative effect of volume expansion while supporting a sufficient number of active sites. Hollow nanofibers are ideal anode materials for LIBs. The hollow structure not only has a large specific surface area, but it acts as a buffer during the lithiation process. The hollow structure can combine numerous components to improve the LIB's performance.

3. Fundamentals of Metal-Ion Batteries

The energy stored in the battery is released when the cathode and anode are connected through an external circuit. The electrolyte, which is a substance that does not conduct electricity but allows the movement of ions, carries the reactant between the two electrodes to prevent the battery from short-circuiting. These three building components can be joined in several ways.

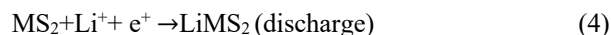
During manufacturing, a polymer membrane separator is used to insulate the electrodes from each other [40]. The reduction of electroactive species in the cathode material and the Li⁺-ion intercalation into accessible locations in the host lattice is involved in the discharge mechanism.

During the discharge process, spontaneous redox reactions cause intercalation at the electrode surface. Electrons are transported from the negatively charged anode to the positively charged cathode via an external circuit to maintain electrical neutrality. When a battery is charged, the cathode releases electrons to the external circuit by desorption of lithium. Common cathode materials include lithium cobalt oxide (LiCoO₂, LCO), lithium iron phosphate (LiFePO₄, LFP), and

lithium manganese oxide (LiMnO₄, LMO). In a typical LIB, the positive and negative electrodes undergo the following chemical reaction as shown in the equations (2) and (3):



Equation (4) depicts the chemical reaction that takes place in a fuel cell during discharge:



Where M=Ti, or Mo

Electrons move from the negatively charged anode to the positively charged cathode via the external circuit to maintain electrical balance. During the recharging process, the flow of ions and electrons is reversed by an external load, returning them to the negative electrode. It is worth noting that in this reversed reaction mode, the electrode that was previously positively charged becomes the anode, while the electrode that was negatively charged becomes the cathode. However, battery researchers commonly refer to the functioning electrode as the cathode, regardless of the operational mode. The charging and discharging processes of an intercalation-based rechargeable battery through the electrodes are summarized in Table 1.

Table 1. The charging and discharging processes of an intercalation-based complete battery involve the flow of ions and electrons through the electrodes.

	Charging	Discharging	Process
Cathode	Intercalation Reduction	De- intercalation Oxidation	Ionic process Electronic process
Anode	De- intercalation Oxidation	Intercalation Reduction	Ionic process Electronic process

Without a significant breakthrough, it is unlikely for Li-ion technology to surpass 300 Wh/kg [41]. As progress in Li-ion material development slows down, alternative chemistries involving alkali intercalation have become more interesting [42-44]. Aquion Energy's sodium-ion batteries [45] are the most advanced among Na-, Mg-, K-, and Ca- batteries. The key advantages of Na-ion batteries over Li-ion batteries are that they have similar (but not identical) electrochemistry and are less expensive. Although the energy density is typically on par with or lower than Li-ion, the increased Na⁺ concentration tends to harm the host lattice more during prolonged cycling [46].

4. Lithium-Intercalation on Battery Characteristics

A successful intercalation battery must meet several requirements simultaneously, regardless of the ion drive. Commercialization, manufacturing, and disposal are all made possible by low-cost, ecologically acceptable raw materials. A high-capacity, high-voltage cathode with outstanding long-term cyclability does not yet exist. While LiFePO₄ exhibits favorable characteristics such as good rate capability, chemical stability, and thermal stability, it has a lower electrochemical potential of 3.5 V and a specific capacity of 170 mAh/g [47,48].

4.1 Capacity

Understanding high-voltage or high-performance materials requires studying both their crystalline and electrical structures. The upper limit of the specific capacity of an intercalating electrode is dictated by the number of electrons that are either gained or lost throughout the cycling process, including the molecular weight of the intercalating substance. Increasing the electrode thickness by minimizing the contribution of all inactive components is a significant technical difficulty [49] that increases the energy density, but leads to reduced power output [50].

4.2 Crystal structure

The fundamental structure of intercalation cathodes consists of a crystal structure containing transition metal centers capable of undergoing redox reactions. This is also generally true for anode materials, except for graphite and other carbon compounds. The majority of effective intercalation materials have a layered structure. Lithiated transition metal oxides such as LiMO_2 (where M might be a mix of Co, Ni, or Mn) [51-53] and graphite-based materials [54] are examples of cathode materials. Other materials including alternate oxides such as MoO_3 [55] or V_2O_5 [56], dichalcogenides such as TiS_2 [57], and developing 2D materials such as MXenes, have also gained significant attention. Spinel structures have a similar structure to layered oxides but with a different arrangement of metal octahedra. LiFePO_4 (LFP) is a controversial material [58], as its performance sometimes exceeds our current understanding. LFP exhibits a significant miscibility gap at equilibrium and $\text{Li}_{0.9}\text{FePO}_4$ and $\text{Li}_{0.1}\text{FePO}_4$ are produced (the precise composition depends on the particle size) [59]. Positively charged cations stabilize the layered oxide structure by opposing the attraction of oxygens in adjacent layers and causing larger interlayer separation. Optimizing many orthogonal aspects of interleaving is a fascinating and challenging part of battery science.

4.3 Voltage

Understanding the chemical potential and interactions between active ions and electrons [60] is crucial for understanding the voltage, making it unnecessary to separate the electronic and ionic components. Conversely, the differentiation of these effects enhances the comprehension of quality. Voltage is mostly affected by the difference in Fermi level between the anode and cathode. Both the chemical potential of interstitial ions in different or crystalline sites and defects that disrupt the local electronic structure affect it. This means that the energy level of the redox pair of this transition metal (or anion, by inference) has a large influence on electrode voltage. By using the ionic radius and Slater's rule, one can determine the amount of oxidizing capacity in a given state of matter for reactive oxygen species. The effective kernel [61] increases electronic binding energy (higher voltage) by adding protons to 3D transition metals.

The first real-world example of an intercalation battery was Whittingham's LiTiS_2 , which was a rechargeable one [62]. The S-3P band has a relatively low voltage (2.6V vs. Li / Li^+) [63], this is one of the main limitations of chalcogenides in general. Because anionic redox has only been documented for oxides, voltage constraints are usually not overcome by increasing capacity. They instead focused on oxides with lower energy bands (the O-2p band), which led to the development of LiCoO_2 (4V) and other cathodes [63,64].

To sum up, capacity and voltage determine the amount of stored energy in a battery. These two characteristics are inextricably linked to the crystal structure and electrical structure of your host material.

4.4 Electronic Conductivity

One of two mechanisms governs electron conduction in electrode materials. At certain Li concentrations, materials such as Li_xCoO_2 and Li_xTiS_2 are metallic conductors [65,66], which contributes to their appealing rate performance. LiFePO_4 (LFP) is characterized by its lack of significant conduction and valence bands, which would enable conduction to be delocalized. The main method of electron transport is the polaron hopping process, which involves the localization of electrons and their subsequent lattice disruption.

Carbon coating is a popular approach for enhancing electronic conductivity that is both scalable and cost-effective [67]. Defect chemistry has also been utilized to anticipate changes in electron and ion conductivity [68,69].

4.5 Ionic Conductivity

The crystal structures of the three types of Li-insertion compounds are shown in Figure 4. Their classification is based on the ion diffusion paths and activation energies that control Li-ion transport in electrode materials [70]. In layered oxides (LiCoO_2), Li^+ migrates through an intermediate tetrahedral location with a minor diffusion barrier (0.3 eV) (see Fig. 4a), and in spinel (LiMn_2O_4), Li moves between tetrahedral sites ($x < 1$) via the Octahedral site (0.4 eV) (See Fig. 4b) [71]. The operating voltage of LFP is lower than that of other positive electrodes (3.45 V vs. Li^+/Li) [72]. Although significant power capabilities of olivine LiFePO_4 were not predicted, Li-ion transport occurs with a low barrier of 0.2 eV along a curved oct-tet-oct trajectory along its b-axis (Fig. 4c) [73].

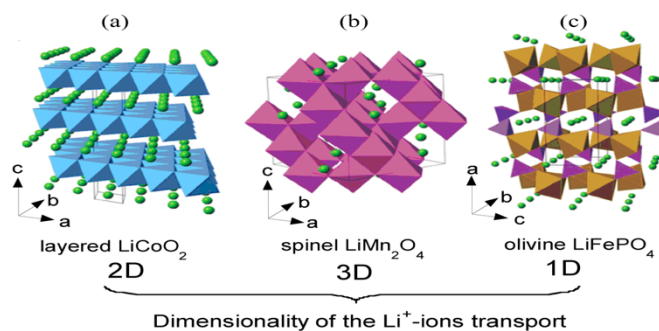


Figure 4. The diffusion pathways for lithium ions include (a) LiCoO_2 , (b) LiMn_2O_4 , and (c) LiFePO_4 [74]

The first-rate performance of LiFePO_4 and the large reported diffusivity raised some questions. LiFePO_4 is an interesting case study in ionic transport [75]. The detection of particle size dependency [76] was one discovery that aided in addressing some of the differences. By lowering particle size, nanoscale [77] (50 nm) LiFePO_4 outperformed bulk. These initiatives are noticeable in two places: enhanced Li-intercalation in xerogel V_2O_5 [78] and improved Mg-insertion in MoS_2 [79]. Another well-known method for increasing power density is to use nanostructures with short diffusion lengths and large surface areas [80,81]. In one recent example, we used electrospun liquid oxygen (LTO) and liquid propylene oxide (LVP) as anode and cathode in a high power density (HPD) battery [82]. Because

the LTO anode has a high voltage of 1.5 V and the cathode has a low capacity of 110 mAh/g, the energy density is low.

4.6 Mechanical tenacity

The dominance of intercalation electrodes in the current market can be attributed to their mechanical stability. Intercalation materials, which undergo volume changes of less than 10% during the cycle, offer advantages over the conversion and alloying reactions in terms of avoiding difficulties [82]. The strain caused by ion insertion and extraction can be accommodated by porous electrodes and other nanostructures [74]. However, selecting an endpoint in cycling reduces strain but also reduces usable capacity and energy density [83].

4.7 Electrochemistry Stability

The electrodes, electrolyte, current collectors, and container of a successful battery must all be compatible. In an ideal scenario, the occurrence of corrosion or chemical degradation would be nonexistent. However, to safeguard a component from further side reactions, it is necessary for chemical, self-limiting passivation layers to form. An exemplary instance of this passivation tendency can be observed in graphite anodes. Batteries with a cathode frequently operate outside of the thermodynamic stability window to generate the greatest voltage feasible [84]. Despite its kinematic limits, oxidation will

eventually deplete energy and power density by irreversibly consuming lithium and building a thicker and more resistant interphase layer. Batteries commonly operate outside the thermodynamic stability window to achieve the maximum feasible voltage on the cathode side.

5. The latest improvement in LIB performance

The revolutionary discoveries resulted in the replacement of the previous era of batteries with a new technology that utilized a CoO₂-cathode and a gasoline coke anode. Notably, John Goodenough, the 2019 Chemistry Laureate, made a critical contribution to quadrupling the capacity of LIBs to 4 volts. This achievement established the groundwork for future growth of considerably more efficient and practical battery systems. Akira Yoshino succeeded in getting rid of natural lithium from the battery and replacing it with lithium ions, which might be more secure than natural lithium. This allowed the battery to be used in practice. Their discovery no longer best enables commercial-scale manufacturing of LIBs but additionally increases studies into a huge variety of the latest technologies, which include wind and solar power. Figure 5 illustrates the layout of the current LIB era advanced via way means of the three scientists.

Table 2. Intercalation electrode materials for rechargeable LIBs.

Type	Cycle life	Working temperature (°C)	Specific Energy (Wh/Kg)	Efficiency (%)	Depth of discharge(%)	Self-discharge rate(% per Month)	Reference
Lead acid	500–5000	–40 –60	35–55	50–75	<70	4–50	[93]
Lithium-ion	1000–20000	–30–55	90–260	~ 95	100	<2	[94]
Na-S	4000–5000	300–350	130–150	75–90	>90	N/A	[95]
Redox flow battery	20,000	10–40	25–40	65–82	100	3-9	[96,97]

Table 3. Various battery systems are compared

	Material	Structure	Average Voltage (V vs. Li)	Practical Capacity (mAh/g)	Date First Reported	Reference
Cathodes	LiCoO ₂	Layered	~3.9	~140	1980	[86]
	LiMn ₂ O ₄	Spinel	~4.1	~120	1983	[87]
	LiFePO ₄	Olivine	~3.45	~160	1997	[88]
	LiNi _{1/3} Mn _{1/3} Co _{1/3} O ₂	Layered	~3.8	~200	2001	[89]
Anodes	LiNi _{0.8} Co _{0.15} Al _{0.05} O ₂	Layered	~3.8	~200	2003	[90]
	Graphite (LiC ₆)	Layered	~0.1	~360	1983	[91]
	Li ₄ Ti ₅ O ₁₂	Spinel	~1.5	~175	1994	[92]

Despite incredibly good efforts and funding on the R&D lever [85], maximum battery progress has occurred at the manufacturing level, presently no longer owing to substance breakthroughs. For LIBs, the most effective five realistic cathode and anode substances have been commercialized to date (Table 2).

The hit elimination of natural lithium from LiCoO₂ in this generation induced a double within the operating voltage and the electrode's overall performance compared to Whittingham's technology. Petroleum coke as anode cloth well-known shows a wide-place section that is heterogeneous, in the main unbiased, and has some related micro areas. The capability of the negative

electrode and cycle performance is enhanced while the cloth's inner shape is more ordered and less complicated to graphitize. Table 3 compares the cycle life, energy density, efficiency, depth of discharge, and self-discharge rate for different types of batteries. The global market for LIBs has grown rapidly due to the surge in demand for electric vehicles in recent years.

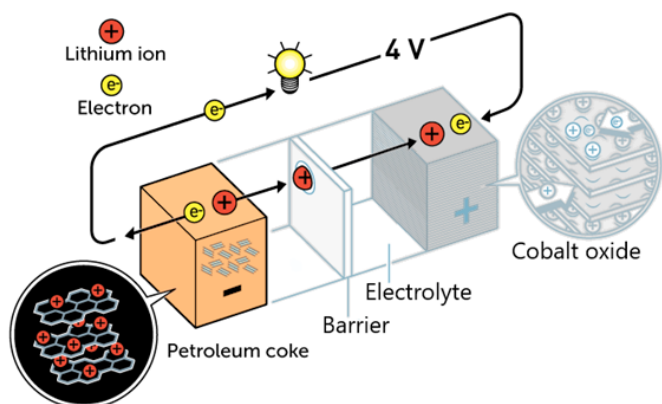


Figure 5. John B. Goodenough's battery with increased cathode potential based on metal oxide [9]

To elaborate on the distinctions between the battery technologies stated above, we have detailed the five significant differences between the four above. The primary differences between flow batteries and LIBs are cost, longevity, power density, safety, and space efficiency. Sodium-ion batteries are a promising replacement for LIBs, which are currently the most used type of rechargeable battery. LIBs offer better efficiency and faster response time than lead-acid and flow batteries. Although LIBs survive longer (they have more charge-discharge cycles than lead-acid batteries), they are typically avoided in low-budget off-grid systems due to their higher cost per kWh of storage capacity [98].

The overall performance parameters of LIBs are largely determined by the electrochemical reactions and the aspect substances utilized in fabricating the batteries, in addition to the mobile engineering and gadget integration involved. The properties of the substances used are determined by the underlying chemistry of the substances. Because of its increased gravimetric power densities of over 250 Wh kg^{-1} and volumetric power densities of less than 650 Wh L^{-1} , Li^+ -ion production is the most prominent current battery technology, which exceeds any competing generation by employing the element of a minimum 2.5V. However, the adoption of LIBs for powering electric-powered motors faces sizeable challenges.

Modern LIBs are restrained to a specific energy density of less than 250 Wh kg^{-1} and a volumetric energy density of $<650 \text{ Wh L}^{-1}$; a boom in those is predicted of up to $\sim 500 \text{ Wh kg}^{-1}$ and over a thousand Wh L^{-1} , respectively. In contrast, these lithium-insertion compounds must have specific characteristics such as chemical stability, capacity, rate capability, toxicity, cost, and safety [99]. Such overall performance parameters in large part depend upon the residences of the anode, cathode, and electrolyte substances employed within the battery system, the given surroundings, and the meaningful use. The strength density of a battery is created from its potential, which is particularly governed by the potential of the high-quality electrode. Simple calculations demonstrate that doubling the potential of the high-quality electrode results in a 57% increase in strength density while increasing the potential of the negative electrode by a factor of ten results in a 47% increase in strength

density. Although intercalation reactions (structure retention) are used in all rechargeable LIBs nowadays, conversion mechanisms should not be disregarded [100]. Conversion reactions are far more powerful than intercalation reactions. Transition metals are another good choice for the construction of anode electrodes for LIBs due to their high theoretical capabilities, low cost, and ease of supply. The development of new compositions and the improvement of electrical conductivity are the primary goals for these materials. Atomic force microscopy (AFM) is another powerful and multipurpose technology that may be utilized to analyze and characterize LIBs with nanometric resolution [101-103]. Increasing surface quality demands and the development of production technologies necessitate a significant investment in both money and effort [104]. This technique also allows for high-resolution examinations of electrochemical processes, current distribution, surface potential, Li-ion transfer, and other surface properties of LIBs [105-108]. Several commercially available electrode materials are compared in various works based on their performance, power, weight, energy storage capabilities, volume, lifetime, and cost [109]. The selection of suitable materials is a difficult issue for researchers. Materials are assessed for two reasons: creating a new product or improving an existing one.

6. Conclusions

Intercalation has enabled LIBs to power our increasingly mobile civilization. LIBs are a well-known group of devices that vary in price, performance, and safety. However, achieving low cost, extended lifespan, excellent performance, and high safety all at the same time is not always possible. The development of low-voltage anodes and high-specific capacity cathodes with high-voltage is a significant barrier to the development of safe, high-energy-density batteries. The performance of materials, particularly the operating voltage, is influenced by the electronegativity and electrical arrangement of the constituent elements. The host lattice's binding strength ensures mechanical, thermal, and cycle stability. The transition metal binary phases that react with lithium via conversion processes have the potential to improve energy density. Although some electrode engineering-based solutions can avoid this problem, the road to long-term cyclability remains long and convoluted. The remarkable voltage hysteresis observed between discharge and charge considerably lowers the round-trip efficiency of the electrode, which is a very significant and generally underestimated obstacle to application. The selection of proper organic solvents is key because they play an important role in increasing Li-ion mobility, which improves the overall performance of the battery cell and is also critical to the device's safety. As a result, manipulating the microstructures, integrating defects, or changing the matter state of a certain material has a direct influence on lithium intercalation into cathode or anode materials that impacts the performance of the entire rechargeable battery. The results of our study emphasize the importance of enhanced energy quality in the development of high-capacity electrode materials, demonstrating how different transition metal ions and appropriate treatment processes can be used to increase the operating voltage of cathode materials. These findings and tactics apply not only to LIBs but can also serve as design principles to stimulate the development of other electrochemical energy storage systems.

Acknowledgements

The authors are thankful to RTE University for the provided facilities.

References

- Theodore, A.M., Konwar, S., Singh, P.K., Mehra, R.M., Kumar, Y. Gupta, M. PEO+NaSCN and ionic liquid-based polymer electrolyte for supercapacitor. *Mater Today Proc* **2020**, 34(3): 802–812
- Theodore, A.M., Promising Cathode Materials for Rechargeable Lithium-Ion Batteries: A Review. *Int. J. Sustain. Energy* **2023**, 14(1):51-58
- Badi, N., Theodore, A.M., Roy, A., Alghamdi, S.A., Alzahrani, A.O. M., and Ignatiev, A. *Int J Electrochem Sci* **2022**, 17, 22064
- Badi, N., Theodore, A.M., Alghamdi, S.A., Al-Aoh, H.A., Lakhout, A., Singh, P.K., Norraahim, M.N.F., Nath, G. The Impact of Polymer Electrolyte Properties on Lithium-Ion Batteries. *Polymers* **2022**, 14, 3101
- Theodore, A.M., Badi, N., Alghamdi, S.A., The Impact of Polymer Electrolyte Properties on Lithium-Ion Batteries. Eliva Press. Global Ltd, **2022**
- Dines, M. B., Lithium intercalation via butyllithium of the layered transition metal dichalcogenides *Mater. Res. Bull.* **1975**, 10(4): 287–291
- Aronson, S., Salzano, F., and Bellafore, D., Thermodynamic Properties of Potassium-Graphite Lamellar Compounds from Solid-State Emf Measurements. *J. Chem. Phys.* **1968**, 49(1):434–439
- Cairns, E.J., and Shimotake, H., High-Temperature Batteries, *Science* **1969**, 164(3886):1347–1355
- Theodore, A. M., Progress into lithium-ion battery research. *J. Chem. Res.* **2023**, 47, 1–9
- Goodenough, J.B., and Park, K.S., The Li-Ion Rechargeable Battery: A Perspective. *J Am Chem Soc* **2013**, 135, 1167–1176
- Van Der Ven, A., Bhattacharya, J., and Anna A. Belak, A.A., Understanding Li diffusion In Li-Intercalation compounds. *Acc. Chem. Res.* **2013**, 46(5):1216-1225
- Yazami, R., Touzain, Ph., A reversible graphite-lithium negative electrode for electrochemical generators. *J Power Sources* **1983**, 9(3):365–371
- Whittingham, M.S., Lithium Batteries and Cathode Materials. *Chem Rev* **2004**, 104(10):4271–4302
- Choi, J.W., and Aurbach, D., Promise and reality of post-lithium-ion batteries with high energy densities). *Nat Rev Mater* **2016**, 1(4):16013
- Goodenough, J.B., and Gao, H., A perspective on the Li-ion battery. *Sci. China Chem* **2019**, 62, 1555–1556
- Thackeray, M. M., Vaughey, J. T., Johnson, C. S., Kropf, A.J., Benedek, R., Fransson, L. M. L., and Edstrom, K., Structural considerations of intermetallic electrodes for lithium batteries *J. Power Sources* **2003**, 113, 124–130
- Timmons, A., and Dahn, J. R. In Situ Optical Observations of Particle Motion in Alloy Negative Electrodes for Li-Ion Batteries *J. Electrochem. Soc.* **2006**, 153(6):1206–1210
- Larcher, D., Beattie, S., Morcrette, M., Edstroem, K., Jumas, J. C., Tarascon, J.M., Recent findings and prospects in the field of pure metals as negative electrodes for Li-ion batteries. *J. Mater. Chem.* **2007**, 17(36):3759-3759
- Inoue, H., Mizutani, S., Ishihara, H., Hatake, S., PRiME **2008**, 214th Meeting of the Electrochemical Society, Honolulu, Hawaii (USA)
- Poizot, P., Laruelle, S., Grugeon, S., Dupont, L., and Tarascon, J. M., Nano-sized transition-metal oxides as negative-electrode materials for lithium-ion batteries. *Nature* **2000**, 407(6803):496-499
- Godshall, N. A., Raistrick, I. D., Huggins, and R. A., *Mater. Res. Bull.* **1980**, 15(5):561–570
- Henriksen, G. L., and Jansen, A. N., *Handbook of Batteries* (Eds. D. Linden and T. B. Reddy), McGraw-Hill, New York, **2002**
- Grugeon, S., Laruelle, S., Dupont, L., and Tarascon, J. M., An update on the reactivity of nanoparticle Co-based compounds towards Li. *Solid State Sci.* **2003**, 5(6): 895–904
- Zhao, Y., Pohl, O., Bhatt, AI., Collis, G.E., Mahon, P.J., Rütther T., Hollenkamp AF., A Review of Battery Market Trends, Second-Life Reuse, and Recycling Sustainable Chemistry, **2021**, 2(1):167–205
- Srinivasan, V., The three laws of batteries (and a Bonus Zeroth Law) *Gigaom*, **2011**
- Crabtree, G., The joint center for energy storage research: a new paradigm for battery research and Development AIP Conf Proc **2014**, 1652, 112–28
- Linden, D., *Handbook of Batteries and Fuel Cells*; McGraw-Hill Book Co.: New York, NY, USA, **1984**, 1075
- Yuan, T., Tan, Z., Ma, C., Yang, J., Ma, Z., Zheng, S., Challenges of Spinel Li₄Ti₅O₁₂for Lithium-Ion Battery Industrial Applications. *Adv. Energy Mater.* **2017**, 7, 1601625
- Ren, W.F., Zhou, Y., Li, J.T., Huang, L., Sun, S.G., Si anode for next-generation lithium-ion battery, *Curr. Opin. Electrochem*, **2019**, 18, 46–54
- Pistoia, G., *Lithium-Ion Batteries: Advances and Applications*; Elsevier: Amsterdam, The Netherlands, **2013**, 664
- Abbas, Q., Mirzaeian, M., Hunt, M.R.C., Hall, P., Raza, R., Current State and Future Prospects for Electrochemical Energy Storage and Conversion Systems. *Energies*, **2020**, 13, 5847
- Whittingham. M. S., Chalcogenide battery, US patent 4,009,052, **1973**
- Goodenough, J. B., and Mizushima, K., Electrochemical cell with new fast ion conductors US patent 4,302,518. **1981**
- Goodenough, J. B., and Park, K. S., The Li-ion rechargeable battery: a perspective. *J. Am. Chem. Soc.* **2013**, 135(4):1167–1176
- Harris, W. S., *Electrochemical studies in cyclic esters Thesis*, University of California, Berkeley, **1958**
- Ramanan, A., Nobel Prize in Chemistry, *Resonance* **2019**, 24, 1381–1395
- Yazami, R., and Touzain, P. J., *Power Sources* **1983**, 9,365–371
- Garche, J., Dyer, C., Moseley, P.T., Ogumi, Z., Rand, D., and Scrosati, B., *Encyclopedia of Electrochemical Power Sources* Ulm: Elsevier B.V., **2009**
- Bruce, P. G., Energy storage beyond the horizon: rechargeable lithium batteries *Solid State Ionics* **2008**, 179, 752–760
- Arora, P., and Zhang, Z., Battery separators, *Chem Rev* **2004**, 104(10):4419–4462
- Thackeray, M.M., Wolverson, C., and Isaacs, E.D., Electrical energy storage for transportation: approaching the limits of, and going beyond, lithium-ion batteries. *Energy Environ*, **2012**, 5(7):785

42. Muldoon, J., Bucur, C.B., Gregory, T., and Johnson, C.S., Quest for nonaqueous multivalent secondary batteries: magnesium and beyond. *Chem Rev* **2014**, 114(23):11683–11720
43. Slater, M.D., Kim, D., and Lee E., et al., Sodium-ion batteries *Adv Funct Mater* **2013**, 23(8):947–958
44. Wang, Y., et al., Emerging non-lithium-ion batteries *Energy Storage Mater* **2016**, 4, 103–129
45. Whitacre, J.F., Wiley, T., Shanbhag, S., Wenzhuo, Y., Mohamed, A., Chun, S.E., Weber, E., Blackwood, D., Lynch-Bell, E., Gulakowski, J., Smith, C., Humphreys, D., An aqueous electrolyte, sodium-ion functional, large-format energy storage device for stationary applications *J Power Sources* **2012**, 213, 255–264
46. Masse, R.C., Uchaker, E., and Cao, G. Beyond Li-ion: electrode materials for sodium- and magnesium-ion batteries. *Sci China Mater* **2015**, 58(9):715–766
47. Yuan, L-X., Wang, Z.-H., Zhang, Hu, X.-L., Chen, J.-T., Huang, Y.-H., and Goodenough, J.B., Development and challenges of LiFePO₄ cathode material for lithium-ion batteries. *Energy Environ Sci* **2011**, 4(2):269–284
48. Wang, J., and Sun, X., Olivine LiFePO₄: The remaining challenges for future energy storage *Energy Environ Sci* **2015**, 8(4): 1110–1138
49. Wood, D.L., Li, J., and Daniel, C., Prospects for reducing the processing cost of lithium-ion batteries. *J Power Sources* **2015**, 275, 234–242
50. Ogihara, N., Itou, Y., Sasaki, T., Takeuchi, Y., Impedance spectroscopy characterization of porous electrodes under different electrode thicknesses using a symmetric cell for high-performance lithium-ion batteries. *J Phys Chem C*, **2015**, 119, 4612–4619
51. Massé, R.C., Liu, C., Li, Y., Mai, L., and Cao, G., Energy storage through intercalation reactions: electrodes for rechargeable batteries, *Natl. Sci. Rev*, **2017**, 4(1):26–53
52. Julien, C.M., Mauger, A., Zaghib, K., and Groult, H., Comparative issues of cathode materials for Li-ion batteries. *Inorganics*, **2014**, 2(1):132–154
53. Manthiram, A., Knight, J.C., Myung, S.T., Oh, S.M., Sun, Y.K., Nickel-rich and lithium-rich layered oxide cathodes: progress and perspectives. *Adv Energy Mater*, **2016**, 6, 1501010
54. Kaskhedikar, N.A., and Maier, J., Lithium storage in carbon nanostructures, *Adv Mater*, **2009**, 21, 2664–2680
55. Hu, X., Zhang, W., Liu, X., Meia, Y., and Huang, Y. Nanostructured Mo-based electrode materials for electrochemical energy storage. *Chem Soc Rev*, **2015**, 44(8):2376–240
56. Liu, Y., Liu, D., Zhang, Q., and Cao, G., Engineering nanostructured electrodes away from equilibrium for lithium-ion batteries. *J Mater Chem*, **2011**, 21, 9969
57. Whittingham, M.S., Electrical energy storage and intercalation chemistry. *Science*, **1976**, 192, 1126–1127
58. Fletcher, S., *Bottled Lightning: Superbatteries, Electric Cars, and the New Lithium Economy* New York: Hill and Wang, **2011**
59. Meethong, N., Huang, H.Y.S., and Carter W.C. et al., Size-dependent lithium miscibility gap in nanoscale Li_{1-x}FePO₄. *Electrochem Solid-State Lett*, **2007**, 10, A134
60. Maier, J., Review—Battery materials: why defect chemistry? *J Electrochem Soc*, **2015**, 162(14):2380–2386
61. Slater, J.C., Atomic shielding constants. *Phys Rev*, **1930**, 36, 57–64
62. Bock, D.C., Marschilok, A.C., Takeuchi, K.J., and Takeuchi, E.S., Batteries used to power implantable biomedical devices *Electrochim Acta*, **2012**, 84, 155–164
63. Scrosati, B., Power sources for portable electronics and hybrid cars: lithium batteries and fuel cells *Chem Rec*, **2005**, 5(5):286–297
64. Park, O.K., Cho, Y., Lee, S., Yoo, H.-C., Song, H.-K., and Cho, J., Who will drive electric vehicles, olivine or spinel? *Energy Environ*, **2011**, 4, 1621
65. Menetrier, M., Saadoun, I., and Levasseur, S., Demas, C., The insulator-metal transition upon lithium deintercalation from LiCoO₂: electronic properties and a ⁷Li NMR study. *J Mater Chem*, **1999**, 9(5):1135–1140
66. Dijkstra, J., Bruggen, C.F.V., Van, and Haas, C., The electronic structure of some monovalent-metal intercalates of TiS₂. *J Phys Condens Matter*, **1989**, 1, 4297–4309
67. Li, H., and Zhou, H., Enhancing the performances of Li-ion batteries by carbon coating: present and future. *Chem Commun*, **2012**, 48, 1201
68. Shin, J.Y., Samuelis, D., and Maier, J., Defect chemistry of lithium storage in TiO₂ as a function of oxygen stoichiometry, *Solid State Ion*, **2012**, 225, 590–593
69. Shin, J., Joo, J.H., Samuelis, D., and Maier, J., Oxygen-deficient TiO_{2-δ} nanoparticles via hydrogen reduction for high-rate capability lithium batteries, *Chem Mater*, **2012**, 24, 543–551
70. Goodenough, J.B., Design considerations. *Solid State Ion.*, **1994**, 69, 184–198
71. Zhang, T., Li, D., Tao, Z., and Chen, J., Understanding electrode materials of rechargeable lithium batteries via DFT calculations. *Prog Nat Sci Mater Int.*, **2013**, 23, 256–272
72. Mayer, S.F., Cristina de la Calle, Fernandez-Diaz, M.T., Amarilla, J. M., and Alonso, J. A., Nitridation effect on lithium iron phosphate cathode for rechargeable batteries. *RSC Adv.*, **2022**, 12, 3696
73. Morgan, D., Van der Ven, A., and Ceder, G., Li conductivity in Li_xMPO₄ (M = Mn, Fe, Co, Ni) olivine materials. *Electrochem Solid-State Lett*, **2004**, 7, 30
74. Liu, Y., Liu, D., Zhang, Q., and Cao, G., Engineering nanostructured electrodes away from equilibrium for lithium-ion batteries. *J Mater Chem*, **2011**, 21, 9969
75. Malik, R., Abdellahi, A., and Ceder, G., A Critical Review of the Li Insertion Mechanisms in LiFePO₄ Electrodes. *J Electrochem Soc*, **2013**, 160, 3179–3197
76. Malik, R., Burch, D., Martin Bazant, M., and Ceder G., Particle size dependence of the ionic diffusivity *Nano Lett*, **2010**, 10, 4123–412
77. Kang, B., and Ceder, G., Battery materials for ultrafast charging and discharging *Nature*, **2009**, 458, 190–193
78. Wang Y, Shang H, Chou T., et al., Effects of thermal annealing on the Li⁺ intercalation properties of V₂O₅ nH₂O xerogel films. *J Phys Chem B*, **2005**, 109, 11361–11366
79. Liang, Y., Yoo, H.D., Li, Y., Shuai, J. Calderon, H.A., Hernandez, F.C.R., Grabow, L.C., and Yao, Y., Interlayer-expanded molybdenum disulfide nanocomposites for electrochemical magnesium storage. *Nano Lett*, **2015**, 15(3):2194–2202

80. Liu, D., and Cao, G., Engineering nanostructured electrodes and fabrication of film electrodes for efficient lithium-ion intercalation *Energy Environ*, **2010**, 3, 1218
81. Wang, Y.W.Y., and Cao, G., Nanostructured materials for advanced Li-Ion rechargeable batteries. *IEEE Nanotechnol Mag*, **2009**, 3, 14–20
82. Liu, C., Wang, S., Zhang, C. Fu, H. Xihui Nan, X., Yang, Y., Cao, G., High-power safety battery with electrospun Li₃V₂(PO₄)₃ cathode and Li₄Ti₅O₁₂ anode with 95% energy efficiency *Energy Storage Mater*, **2016**, 5, 93–102
83. Mukhopadhyay, A., and Sheldon, B.W., Deformation and stress in electrode materials for Li-ion batteries. *Prog Mater*, **2014**, 63, 58–116
84. Winter, M., Besenhard, J.O., Spahr, M.E., Novak, P., Insertion electrode materials for rechargeable lithium batteries. *Adv Mater*, **1998**, 10, 725–63
85. Crabtree G., The joint center for energy storage research: a new paradigm for battery research and development *AIP Conf Proc*, **2014**, 1652, 112–28
86. Mizushima, K., Jones, P.C., Wiseman, P., and J.B., Goodenough Li_xCoO₂ (0<x<1): a new cathode material for batteries of high energy density, *Mater Res Bull*, **1980**, 15, 783–789
87. Thackeray, M.M., David, W.I.F., Bruce, P.G., and Goodenough J.B., Lithium insertion into manganese spinels *Mater Res Bull*, **1983**, 18, 461–72
88. Padhi, A.K., Nanjundaswamy, K.S., and Goodenough, J.B., Phospho-olivines as positive-electrode materials for rechargeable lithium batteries *J Electrochem Soc*, **1997**, 144, 1188
89. Ohzuku, T., Makimura, Y., Layered lithium insertion material of LiCo_{1/3}Ni_{1/3}Mn_{1/3}O₂ for lithium-ion batteries. *Chem Lett*, **2001**, 30, 642–643
90. Albrecht, S., Kumper, J., Krufft, M., Malcus, S., Vogler, C., Wahl M., and Wohlfahrt-Mehrens, M., Electrochemical and thermal behaviour of aluminum- and magnesium-doped spherical lithium nickel cobalt mixed oxides Li_{1-x}(Ni_{1-y-z}Co_yM_z)O₂ (M = Al, Mg). *J. Power Sources*, **2003**, 119, 178–83
91. Yazami, R., Touzain, P., A reversible graphite-lithium negative electrode for electrochemical generators. *J. Power Sources*, **1983**, 9, 365–37
92. Ferg, E., Gummow, R.J., Dekock, A., and Thackeray, M.M., Spinel anodes for lithium-ion batteries *J Electrochem Soc*, **1994**, 141, L147–L150
93. Koontz, D.E., Feder, D.O., Babusci, L.D., and Luer, H.J., Lead-acid battery: reserve batteries for bell system use; design of the new cell *Bell System Technical J.*, **1970**, 49, 1253–1278
94. Huang, B., Pan, Z., Su, X., and An, L., Recycling of lithium-ion batteries: recent advances and perspectives. *J Power Sources*, **2018**, 399, 274–286
95. James M.-I., Recent advances on flexible electrodes for Na-ion batteries and Li-S batteries *J Energy Chem*, **2019**, 32, 15–44
96. Ghimire, P.C., Bhattarai, A., Schweiss, R. Scherer, G.G., Wai N., and Yan, Q., A comprehensive study of electrode compression effects in all vanadium redox flow batteries, including locally resolved measurements *Appl Energy*, **2018**, 230, 974–982
97. Baumann, L., and Bogasch, E., Experimental assessment of hydrogen systems and vanadium-redox-flow batteries for increasing the self-consumption of photovoltaic energy in buildings. *Int J Hydrogen Energy*, **2016**, 41, 740–751
98. Keshan, H., Thornburg, J., Ustun, T.S., Comparison of lead-acid and lithium-ion batteries for stationary storage in off-grid energy systems. Conference: 4th IET Clean Energy and Technology Conference (CEAT 2016) **2016**, 1–7
99. Theodore, A. M., Abdullahi, A.A., Pawan, S. D., Effect of Layered, Spinel, and Olivine-Based Positive Electrode Materials on Rechargeable Lithium-Ion Batteries: A Review. *JCMPS*, **2023**, 6, 38–57
100. Wang, F., Robert, R., Chernova, N.A., Omenya, F., Badway, F., Hua, X., Ruotolo, M., Zhang, R., Wu, L., Volkov, V., Su, D., Key, B., Whittingham, M.S., Grey, C.P. Amatucci, G.G., Zhu, Y., and Graetz, J., Conversion reaction mechanisms in lithium-ion batteries: study of the binary metal fluoride electrodes. *J Am Chem Soc*, **2011**, 133, 18828–36
101. Danis, L., Gateman, S.M., Kuss, C., Schougaard, S.B., Mauzeroll, J., Nanoscale measurements of Lithium-ion-battery materials using scanning probe techniques, *ChemElectroChem*, **2017**, 4, 6–19
102. Tennyson, E.M., Gong, C., Leite, M.S., Imaging energy harvesting and storage systems at the Nanoscale, *ACS Energy Lett*, **2017**, 2, 2761–2777
103. Huang, S.Q., Wang, S.W., Jin, Y. Wang, D., Shen, C., Application of Atomic Force Microscopy for the study of lithium-ion batteries. *J. NanoScience, NanoEngineering Appl.*, **2015**, 5, 35–47
104. Eyercioglu, O., Gov, K., and Aksoy, A., Validation of material model and mechanism of material removal in abrasive flow machining, *The International Journal of Materials and Engineering Technology (TIJMET)*, **2023**, 6(1):7-11
105. Liu, X., Wang, D., Wan, L., Progress of electrode/electrolyte interfacial investigation of Li-ion batteries via in situ scanning probe microscopy, *Sci. Bulletin*, **2015**, 60, 839–849
106. Zhiqiang, Z., Yuxin, T., Zhisheng, L., Jiaqi, W., Yanyan, Z., Renheng, W., Wei, Z., Huarong, X., Mingzheng, G., Xiaodong, C., Fluoroethylene Carbonate enabling a robust LiF-rich solid electrolyte interphase to enhance the stability of the MoS₂ Anode for Lithium-ion storage, *Angewandte Chemie International Edition*, **2018**, 57, 3656–3660
107. Lu, W., Xiao, J., Wong, L.-M., Wang, S., Zeng, K., Probing the ionic and electrochemical phenomena during resistive switching of NiO Thin Films, *ACS Appl. Mater. Interfaces*, **2018**, 10, 8092–8101
108. Zhu, K., Luo, Y., Zhao, F., Hou, J., Wang, X., Ma, H., Wu, H., Zhang, Y., Jiang, K., Fan, S., Wang, J., Liu, K., Free-standing, binder-free Titania/super-aligned carbon nanotube anodes for flexible and fast-charging Li-ion batteries. *ACS Sustainable Chem. Eng.*, **2018**, 6, 3426–3433
109. Aktürk, A., Seda Türk, S., Comparison of An Interval Type-2 Fuzzy Sets and AHP Methods For Material Selection Problem on Lithium-Ion Batteries, *The International Journal of Materials and Engineering Technology (TIJMET)*, **2020**, 3(1):30-46