

Review on Performance of Lithium Titanate and Its Impurities Dopant as a Lithium-Ion Battery Anode

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ABSTRACT

Li-ion batteries are the main source of energy for electronic devices such as cameras, calculators, mobile phones, laptops, and electric vehicles. Among the materials being considered, lithium titanate ($Li_4Ti_5O_{12}$) has become a promising anode material due to its high stability and safety, as well as enabling high operability without sacrificing lifetime. However, in order to further improve performance and customise properties for specific applications, impurity dopants have been investigated as a means of modifying $Li_4Ti_5O_{12}$ performance. This paper examines $Li_4Ti_5O_{12}$ and its impurities as anode materials. Starting with a basic understanding of the crystal structure and characteristics of $Li_4Ti_5O_{12}$, its properties and applications. Besides, this study explores the effects of different dopants on the $Li_4Ti_5O_{12}$ on battery parameters. Based on various research studies and recent developments, the review summarises the current knowledge about $Li_4Ti_5O_{12}$ and impurity dopants. Each dopant's different effects on the lattice structure highlight its importance for further development. As a result, it may lead to future research of $Li_4Ti_5O_{12}$ anodes for large-scale energy storage technology.

Keywords: Lithium-ion batteries, Anode performance, Lithium titanate, Impurities dopant

1. INTRODUCTION

Li-ion batteries have attracted much attention in recent decades as one of the most advanced rechargeable batteries. They are currently the primary source of power for electronic devices such as cameras, calculators, mobile phones, laptops, and even electric vehicles (EVs). Li-ion batteries are used because of their advantages over other types of batteries, such as no need for storage or scheduled cycling to extend battery life, high specific capacity and voltage, and high energy density [1], [2].

The working principle of lithium-ion batteries is to transform chemical energy into electrical energy through electrochemical processes [3]. Its components consist of electrodes (cathode and anode), electrolytes, and separators. It is known that the electrolyte and the separator themselves act as a bridge for the lithium ions, ensuring that they flow and avoid short circuits. Each electrode is connected to the electrical circuit in its basic configuration. Naturally, during the charging mode, there is a deintercalation process where the cathode will undergo an oxidation reaction, which initially had neutral lithium turned into Li^+ ions and will release the electrons. These Li^+ ions then move to the anode through the electrolyte, while the electrons will be transferred through the external device. As a result, the electrons obtained cause a reduction reaction in the anode material. Nevertheless, since lithium

ions are involved in the reaction of both electrodes, the battery can be recharged by the reverse interaction, i.e., discharging mode (anode to cathode), as shown in Figure 1 [4], [5], [6].

The current fabrication of cathode materials is lithium cobalt oxide ($LiCoO_2$), lithium manganese oxide ($LiMn_2O_4$, LMN), lithium nickel manganese cobalt oxide ($LiNiMnCoO_2$, NMC), and lithium iron phosphate ($LiFe_2PO_4$, LFP). Whereas anode materials use carbon-based materials such as graphite, carbon nanotubes, graphene, etc. [2], [7]. In fact, carbon in the form of graphite is the most commonly used as an anode material in lithium-ion batteries. The electrochemical activity of graphite is based on the

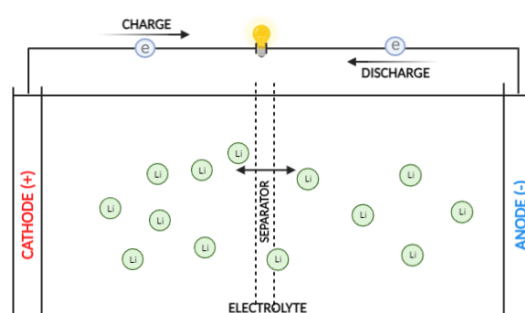


Figure 1. Working principle of a Li-ion battery

intercalation and deintercalation of Li^+ ions in its layered structure [8]. However, the intercalation of Li^+ ions in graphite occurs at a potential of $\sim 0.1 V$ vs. Li^+/Li . Such a low potential favors the reduction of organic electrolytes and leads to the formation of a solid electrolyte interface (SEI) layer on the graphite surface, which results in the consumption of active Li^+ ions during its formation and may act as a barrier to the back-and-forth movement of Li^+ ions [9], [10], leading to dendrite formation. During charging mode, dendrite formation begins at the anode and continues to the battery's cathode. If dendrite production continues for a long time, it may lead to significant thermal runaway in the lithium-ion battery, making it unsafe [11]. Sun *et al.* also revealed that during lithium intercalation and deintercalation, a solid electrolyte interface (SEI) film usually forms at potentials below $0.8 V$ vs Li^+/Li [12]. However, advanced Li-ion batteries based on graphite anode materials are challenging to meet the requirements of such large-scale, high-capacity applications due to power density and safety performance limitations. Therefore, finding other candidates besides traditional commercial graphite is recommended [13].

In the last decade, significant efforts have been focused on exploring advanced anode materials with superior electrochemical properties to replace traditional graphite-based anodes that may be able to overcome graphite's limitations. One material that shows promising potential is lithium titanate ($Li_4Ti_5O_{12}$). Several previous reviews have discussed $Li_4Ti_5O_{12}$ anode materials, covering topics such as structure, battery safety issues, synthesis methods, and electrochemical performance [9], [12] [1]. However, the aim of this review is to provide an overview of lithium titanate and discuss the challenges and improvement opportunities or methods related to this material, particularly in investigating the performance of $Li_4Ti_5O_{12}$ and its impurity dopants as Li-ion batteries anodes.

2. ALTERNATIVE ANODE MATERIAL: $Li_4Ti_5O_{12}$

Another material that can play a role as an anode and as a replacement for graphite is lithium titanate ($Li_4Ti_5O_{12}$). In the previous study, spinel $Li_4Ti_5O_{12}$ is a type of material that is commonly used as a battery due to its excellent performance, reduced risk of dendrite formation [14]; [15] and is recognised as a safe alternative material [16]. The structure and specific characteristics of lithium titanate as an anode material, as well as its properties and applications, will be presented in the following sections. In addition, a discussion on battery parameters and lithium titanate anode performance is also given.

2.1. Structure and Characteristics of $Li_4Ti_5O_{12}$

$Li_4Ti_5O_{12}$ has a face-centred cubic spinel structure with an $Fd\bar{3}m$ space group [9], where the octahedral site 16d is randomly occupied by lithium and titanium, the tetrahedral site 8a is occupied by lithium only, and site 16c is vacant. Basically, Li^+ ions at the initial stage of the insertion (discharge) process, three lithium ions from 8a will move to site 16c. During the (charging) process, lithium ions are extracted from site 16c through site 8a, and other lithium ions return to site 8a from site 16c [12], [17].

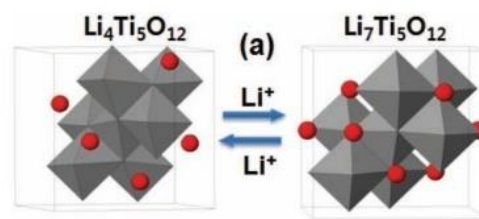
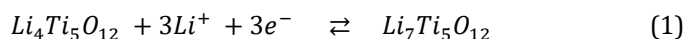


Figure 2. Structure of Structure of $Li_4Ti_5O_{12}$ and $Li_7Ti_5O_{12}$, showing no volume change after charge-discharge [19].

Furthermore, it is generally believed that during normal discharge over $1.0 V$, $Li_4Ti_5O_{12}$ goes through a two-phase transformation from $Li_4Ti_5O_{12}$ and $Li_7Ti_5O_{12}$ (rock salt structure; space group $Fm\bar{3}m$) which leads it to be stable as shown in Figure 2, with a volume change as shown in Figure 2 of only 0.2%, which is negligible, hence referred to as “zero strain” material [18], [19], [20].

In the following equation, the working principle is that Li^+ will diffuse from the electrolyte solution, and then a charge transfer reaction occurs on the surface of the $Li_4Ti_5O_{12}$ particle/electrolyte interface accompanied by electron acceptance, then Li^+ will diffuse into the $Li_4Ti_5O_{12}$ [21]. Whereby one $Li_4Ti_5O_{12}$ mole can accommodate 3 mol of Li^+ , resulting in a theoretical specific capacity of $165 mAh/g$. Since it accommodates 3 moles of Li^+ during the charging/discharging process, it will not affect the structural stability, or it can be mentioned that there is no irreversible capacity loss during the initial charge and discharge cycle, and as long as the Li^+ ion insertion process occurs, $Li_4Ti_5O_{12}$ may undergo negligible volume changes [22], [20], [16].



The study by Ohzuku *et al.* presented the lattice parameter obtained as $a = 8.365 \text{ \AA}$ and indicated that the lattice dimensions also do not change during charge and discharge. Besides that, due to Li^+ ions have the same size as the lattice in the $Li_4Ti_5O_{12}$ structure, which helps maintain the stability of the $Li_4Ti_5O_{12}$ structure with fewer particles experiencing fatigue during the charge-discharge process. It shows a flat voltage plateau at around $1.55 V$ vs. Li/Li^+ , as it is considered a two-phase process between $Li_4Ti_5O_{12}$ and $Li_7Ti_5O_{12}$ [23]. It is well above the voltage for interfacial solid electrolyte (SEI) layer formation and lithium dendrite growth (at $\sim 0.8 V$), ensuring the battery's safety when in use [14].

2.2. Properties and Applications of $Li_4Ti_5O_{12}$

$Li_4Ti_5O_{12}$ is an attractive material with several desirable properties that can be exploited in various applications. $Li_4Ti_5O_{12}$ exhibits a flat voltage profile, as mentioned earlier, which signifies that its voltage remains relatively constant throughout most of the charge and discharge process. This flat voltage characteristic is beneficial as it prevents overcharging and over discharging, thus improving the safety and lifetime of Li-ion batteries. In addition, the intrinsic stability of lithium titanate ($Li_4Ti_5O_{12}$) allows operation in extreme temperatures (from $-50^\circ C$ to $+65^\circ C$) without sacrificing lifetime, which

cannot be achieved by most other lithium cells [14]. Further details on the properties and the factor of $Li_4Ti_5O_{12}$ are summarised in Table 1. Besides electric vehicles and grid energy storage, as previously described, $Li_4Ti_5O_{12}$ is also being considered for new applications. For example, $Li_4Ti_5O_{12}$ is being explored in high-power devices, such as industrial equipment, where safety, durability, and fast charging are critical. In addition, the stability of $Li_4Ti_5O_{12}$ in extreme temperatures and long cycle life make it suitable for defense applications, such as satellites and unmanned aerial vehicles (UAVs) [24], [25].

At the same time, compared with other anode materials, spinel $Li_4Ti_5O_{12}$ is cheaper and easier to fabricate than alloy-based anodes and has better electrochemical performance and higher safety than carbon anodes in lithium-ion batteries [32]. The comparison between spinel lithium titanate and other anode materials is shown in Table 2.

Besides, the formation of SEI and dendrites can be prevented by $Li_4Ti_5O_{12}$ material. It should be noted that $Li_4Ti_5O_{12}$ spinel has been widely known to have a lower theoretical specific capacity of (165 mAh/g) compared to graphite, which is about 372 mAh/g [45]. This limitation results in a trade-off between specific capacity and high-speed capability. Therefore, the choice of $Li_4Ti_5O_{12}$ as an anode material depends on the specific needs of the application, where safety and high performance are more

important than achieving the highest energy density. At the same time, researchers have explored various strategies to improve the performance of $Li_4Ti_5O_{12}$, with some approaches through nanostructured, surface modifications or composites [46], [47], [16].

Nano-sized particles are one of the strategies to improve the electrochemical performance of electrode material. The nanostructure can be attributed to the shortened Li^+ transport path and enlarged access area of the electrolyte, so that it has a very fast charge/discharge capability [48]. In the sample preparation at the micro/nanoscale, it can improve the electrical conductivity and increase the tap density, and it is often used to modify the surface of the $Li_4Ti_5O_{12}$ itself. In addition, reducing the size of carbon, rGO, copper, etc., which are highly dispersed on the particle surface (in the size range of 4 – 200 nm), can improve the contact between $Li_4Ti_5O_{12}$ particles through the wet chemical route, thereby improving its rate performance.

On the other hand, it was discovered that increasing the carbon content itself can enhance the rate capability. However, the higher carbon content in $Li_4Ti_5O_{12}$ /carbon nanocomposites is undesirable as it leads to lower tap and less material in the electrode. Additionally, the nano-sized composite can be attributed to the shortened Li^+ transport path and enlarged access area, which allow the electrolyte to have a very fast charge/discharge capability [48], [49], [50].

Table 1. Properties and Applications of $Li_4Ti_5O_{12}$

No.	Properties	Factors	Applications	References
1.	High safety and thermal stability	It has a stable working voltage of 1.55 V, resulting in no dendrite growth, and Li^+ ions have the same size as the lattice parameter.	Electric vehicles, large stationary power sources	[26], [27], [28]
2.	Long cycle life and high-rate capability	Small volume change, "zero strain," is the key factor of their excellent cyclability and high coulombic efficiency (nearly 100%) at 1 C.	Energy storage systems, smart grids.	[29], [14], [16]
3.	Wide operating temperatures range	The intrinsic stability of Lithium titanate ($Li_4Ti_5O_{12}$) allows operation from $-50^\circ C$ to $+65^\circ C$, without sacrificing lifetime, which cannot be achieved by most other lithium cells.	Electrochemical energy storage system for renewable electricity.	[14], [30], [31]
4.	Environmental friendliness	Non-toxic and cheap	Satellites, aerospace and could play an essential role in future clean energy systems.	[27]

Table 2. Comparison of performance for other anode materials

Anode Materials	Theoretical, Practical Capacity (mAh/g)	Coulombic Efficiency (%)	Cycle Stability (cycles)	References
Graphite	372, 311	99.16	100	[30], [33]
Graphene	540-945	99.0	20, 200	[34], [27], [36]
Graphene Oxide	456	-	200	[37]
Si	3578	-	-	[38]
Alloy materials: Germanium (Ge) Sn, $Li_{22}Sn_5$ Ag	>1000 994 248	>95	250-1200	[36], [39], [40]
TiO_2	335, 314	88	100	[41], [42]
$Li_4Ti_5O_{12}$	150-165	~100	70, 250	[43], [44], [16]

Another way to improve the electrical conductivity of $Li_4Ti_5O_{12}$ is to perform surface modification. Carbon coating is a common approach for surface modification to enhance electrochemical performance, including rate capability and cycle stability. Due to its high electronic conductivity and good chemical stability, this coating improves interparticle contact and contributes to forming a homogeneous SEI layer on the surface of the active particles, thereby reducing side reactions. As discussed by Cheng *et al.* carbon-coated $Li_4Ti_5O_{12}$ improves the surface electrical conductivity and contact with the electrolyte solution, leading to significantly enhanced electrochemical performance; where carbon has access to electrons and Li ions at every point of the particle surface, it can present much higher reaction rates than $Li_4Ti_5O_{12}$. In this study, it has also been explained that the optimal condition for $Li_4Ti_5O_{12}$ coating (thermal vapour decomposition TVD method) is at $800^\circ C$, with an $Li_4Ti_5O_{12}$ /carbon capacity of $160 mAh/g$ obtained based on the weight of the composite material, i.e., carbon is slightly lower than $Li_4Ti_5O_{12}$ and the $800^\circ C$ $Li_4Ti_5O_{12}/C$ sample shows good rate capability, even at a discharge rate of $24C$ [21]. Sakai *et al.* (2020) prepared $Li_4Ti_5O_{12}$ powder coated with aluminium fluoride (AlF_3), and placed it in an Ar atmosphere at $400^\circ C$ for 2 hours. The amount of aluminium fluoride coating was controlled at 1 and 5 wt% by the weight of $Li_4Ti_5O_{12}$ powder. The results showed that at a surface modification of 5% AlF_3 - $Li_4Ti_5O_{12}$ experienced a sharp decrease in charge/discharge capacity. While at 1% AlF_3 - $Li_4Ti_5O_{12}$ gives a stable discharge capacity of about $160 mAh/g$ after 50 cycles. It is due to the surface layer component exceeding the required amount and partially reacting with the aqueous solution, which makes it a resistance layer and inhibits the insertion/deinsertion of lithium ions. Therefore, the ratio control to modify the surface is also very influential [51].

Additionally, it is known that conventional Li-ion batteries consist of electrodes, which can act as electrode composites because a large amount of binder and conductive additives are added to the active material with the purpose of the adhesion of the electrode to the current collector as well as improving the current collection efficiency. Therefore, carbon-coated $Li_4Ti_5O_{12}$ can also be referred to as a composite electrode, which has a certain core-shell morphological structure with a low content of the second material, usually less than five wt%. Another advantage of these composite electrodes is that the second material used can also act as a support in improving the mechanical properties of the electrode so that the amount of binder can be reduced or even completely eliminated, which can improve the gravimetric energy density, operational safety, and service life of the electrode because side reactions between the binder and other additives in the electrolyte liquid can be minimised or avoided. Furthermore, the electronic conductivity of lithium-ions can also be improved [52].

However, it can be said that the current anode materials make it challenging to meet the above requirements simultaneously. Therefore, the recent research on anode materials for lithium-ion batteries focuses on how to increase the energy storage capacity of materials, reduce

the irreversible capacity of the first charge, improve cycle performance and safety, and reduce the cost. Based on the above study results, it can be seen that the mixing of more than one material with small-scale particle size can improve the electrochemical properties of $Li_4Ti_5O_{12}$ itself, compared to pure $Li_4Ti_5O_{12}$ (which has a theoretical specific capacity value of $165 mAh/g$). Ultimately, the capability of $Li_4Ti_5O_{12}$ as a battery storage application has many factors. In addition, it is mentioned that the synthesis method dramatically affects the morphology and electrochemical performance of the obtained $Li_4Ti_5O_{12}$ materials. Even the same material produced by different processes has different morphology, structure, particle size, and electrochemical properties. At the same time, using the same preparation process, the performance of synthetic materials will be affected by many factors, such as the lithium-titanium ratio, reaction temperature, reaction time, reaction gas atmospheric environment, etc. [27]. Each development method, such as nanostructures, surface modifications, and composites, has its advantages and disadvantages, and it can be concluded that the best choice basically also depends on the specific purpose and conditions. It is important to carry out further research, characterisation, and optimisation of each method to ensure maximum performance improvement and to achieve the expected results in $Li_4Ti_5O_{12}$ development.

3. THE IMPURITIES DOPING IN $Li_4Ti_5O_{12}$

Naturally, impurity doping involves the intentional introduction of small amounts of elements with different materials (impurities) into the crystal lattice of a material to modify its properties. In the context of $Li_4Ti_5O_{12}$, the researchers investigated the effects of various impurity dopants on its electrochemical performance as an anode material for lithium-ion batteries. These dopants can modify the structural, electron, and ionic transport properties of $Li_4Ti_5O_{12}$, thereby improving the specific capacity, rate capability, and overall electrochemical stability. On the other hand, Ezhyeh *et al.* mentioned that elemental doping is one of the efficient ways to improve the performance of $Li_4Ti_5O_{12}$. These stimulants work by changing the bonding strength, local environment of the lattice, valence state of positive ions, and lattice defects. At the same time, doping causes changes in the host lattice structure and creates new defects or gaps. The lattice structure's resistance to ion migration changes, as does the ion diffusion coefficient. To improve the electronic and ionic conductivity of $Li_4Ti_5O_{12}$, extensive doping studies have been conducted, including replacing the tetrahedral Li site 8a, the octahedral Ti site 16d, the O site 32e, or a combination of these sites. There are several types of impurity dopants that have been investigated for doping lithium titanate anodes. A few examples of the types of ions that can be selected as dopants include metallic doping (such as Al, Ba, Bi, Ca, Ce, Fe, Cu, etc.), non-metallic doping (such as Br, F, and N), and co-doping (such as Al/Mg , Al/Mn , La/F , etc.) [53].

3.1. Impact of Doping on Battery Parameters

However, to assess the suitability of lithium titanate through doping as an anode material, understanding the

electrochemical performance characteristics of the resulting battery is essential. Several parameters in this assessment need to be known to optimise the design of Li-ion batteries as an anode and identify areas for potential improvements, such as specific capacity and rate capability (C-rate), energy density, coulombic efficiency, and cycle life.

3.1.1. Specific Capacity

Specific capacity is defined as the amount of energy or electric charge that can be stored by a battery in units of mass [54], which is measured in, Wh/g or Ah/g , known as gravimetric energy density. For example, research studies conducted by Johnson *et al.* synthesised $Li_4Ti_5O_{12}$ anodes by investigating the specific capacity of a lithium-ion cell. A specific capacity of 160 mAh/g was achieved. This indicates that the battery could store 160 milliampere-hours of charge per gramme of $Li_4Ti_5O_{12}$ in the anode. Several studies have highlighted the potential for dopants to significantly increase specific capacitance [16]. For example, Zou *et al.* showed that doping treatment of $Li_4Ti_5O_{12}$ resulted in an increase in specific capacitance, with capacities ranging from 235.7 mAh/g to 200.8 mAh/g [55]. Deng *et al.* also obtained a high-capacity value of 216.4 mAh/g , compared to the capacity of pure $Li_4Ti_5O_{12}$, which is 167.5 mAh/g at 1C, respectively. This increase can be attributed to the occurrence of structural changes due to the presence of impurities in the $Li_4Ti_5O_{12}$ structure itself, as previously described [33]. A high specific capacity indicates that the battery can store more energy per unit mass or volume, resulting in a more durable and higher-capacity energy storage system [16].

3.1.2. Rate Capability (C-rate)

Rate capability is an important parameter for characterizing a battery's charge and discharge capability. It refers to the ability of a battery to provide or receive a charge at a specified rate without significantly degrading performance. Charge-discharge capability is often expressed in C-rate and is used in evaluating current for battery testing or operation. In theory, 1C-rate refers to the current that consumes all the capacity within one hour. Batteries rarely reach their theoretical capacity within one hour due to polarisation associated with internal resistance, such as ohmic and electrochemical resistance. Therefore, in practical applications, the 1C capacitance is usually realised with a low current density (such as $C/10$ or $C/20$), and the resulting 1C capacitance is used to determine the corresponding 1C rate. Since a lower C-rate means a slower charge, each of $C/10$, $C/2$, and 1C take 10 hours, 2 hours, and 1 hour, respectively. The rated capacity can be determined by the capacity obtained at a high C-rate compared to the capacity at a low C-rate and is broadly defined by its theoretical capacity value [56]. The doping of $Li_4Ti_5O_{12}$ with specific elements, such as Mo^{6+} , has been investigated by Maiti *et al.* to improve its C-rate capability. This section describes the role of Mo^{6+} doping in facilitating faster lithium-ion transport within the $Li_4Ti_5O_{12}$ lattice. The incorporation of Mo^{6+} ions can modify the structural and kinetic properties of the material, leading to an improvement in the rate performance of doped $Li_4Ti_5O_{12}$ [57].

3.1.3. Energy Density

Energy density is often defined as the amount of energy a battery contains relative to its size, also known as volumetric energy density. Energy density is typically measured in Wh/L or Ah/L . To increase the volumetric energy density, the amount of inactive material must be minimized so that more active material can be incorporated into the electrode at a fixed volume. In particular, the amount of electrolyte must be reduced to a level that does not damage the electrochemical performance at the electrodes. However, compared to gravimetric energy density or specific capacity, volumetric energy density is more difficult to calculate because the electrode density is determined by the active and inactive redox materials [58].

3.1.4. Coulomb Efficiency

Coulomb efficiency is one of the most important characteristics to recognise, as it can indicate the ratio of the discharging capacity to the charging capacity of a particular electrode in a cell. The ideal coulomb efficiency value is 100%, which means that every lithium-ion that leaves the cathode in a fully charged state can return to the cathode in an empty state. However, in each cycle, some lithium is consumed due to side reactions trapped in the SEI formation. For example, $Li_4Ti_5O_{12}$ material has a higher working voltage of 1.55 V, which is far above the SEI formation and lithium dendrite growth, thus ensuring the safety of the battery during use, as mentioned earlier. A high coulomb efficiency is essential for the long-term stability of lithium-ion batteries, especially for applications that require long life and consistent performance, as obtained by Xu *et al.* in which the coulomb efficiency can remain stable at $\geq 98\%$ after 1000 cycles [59]. Normally, the standard service life of energy storage equipment in the electric vehicle industry is 80%. Therefore, it is crucial to consider the experimental factors that must be controlled to precisely measure the coulombic efficiency during charging and discharging [60].

3.1.5. Cycle Life

Cyclability is a measure of how often the electrode material maintains its original capacity during cycling. Galvanostatic charge/discharge is the standard method for evaluating cycling stability. Excellent cycling performance necessitates active materials with high structural stability against electrochemical strain and volume changes, as well as a stable electrolyte-electrode interface that allows reversible ion transfer at each cycle without lithium loss, which is related to their coulombic efficiency value [54]. A recent study by Deng *et al.* showed excellent cycle stability, with capacity remaining high (180.6 mAh/g) even after 500 cycles. In addition, the coulombic efficiency of Cu-doped $Li_4Ti_5O_{12}$ almost always reaches 99.9%. It is explained that this is due to the Cu^{2+} doping, which can create abundant oxygen vacancies, thus storing excess lithium ions and improving electronic conductivity with low charge transfer resistance. Another factor is the sample's porous structure, which has a large specific surface area [61]. Besides, O.V. *et al.* on the synthesis of germanium-doped $Li_4Ti_5O_{12}$ ($Li_4Ge_xTi_{5-x}O_{12}$). The investigation showed that

germanium doping of $Li_4Ti_5O_{12}$ effectively increases the lifetime of Li-ion batteries. The incorporation of germanium into the $Li_4Ti_5O_{12}$ lattice does not cause any stress or deformation in the $Li_4Ti_5O_{12}$ lattice, so germanium can facilitate the diffusion of lithium ions and also improve the ionic mobility. This germanium doping process reduces the stress on the material during charge and discharge cycles, which contributes to increased lifetime [62]. It is also known that a stable SEI plays an essential role in achieving high initial Coulombic efficiency. A greater coulombic efficiency indicates a longer battery life cycle [63].

3.2. Impact of Various Dopants on Anode Performance

The introduction of dopant impurities into the lithium titanate lattice can have various effects on its performance as an anode material. In the following section, various types of impurity dopants used in lithium titanate anode materials have been investigated, and some other studies are listed in Table 3.

3.2.1. Metallic Doping

First of all, in the study of F. Li *et al.* the preparation of Mg-doped $Li_4Ti_5O_{12}$ (nanoparticles, 200 nm) was carried out with a solid-state reaction route at $800^\circ C$ for 8 h in water. This study aims to determine the effect of nano-sized materials and Mg^{2+} doping on the electrochemical performance of $Li_4Ti_5O_{12}$. However, a charge-discharge cycling test and EIS analysis were performed to study their electrochemical performance. The test results show that the doped $Li_4Ti_5O_{12}$ has excellent electrochemical performance, having obtained an initial discharge capacity of $190 mAh/g$ at 1C and even after 100 cycles at 5C, it still produces a capacity of $150 mAh/g$. While the undoped electrode only showed a discharge capacity of about $134 mAh/g$. Thus, the Mg- $Li_4Ti_5O_{12}$ electrode obtained from the solid-state reaction method can be considered a promising anode material for high-performance Li-ion batteries [75].

In addition to Mg^{2+} , Priyono *et al.* have also doped $Li_4Ti_5O_{12}$ with Ca^{2+} to improve the performance of $Li_4Ti_5O_{12}$ anodes. In this study, the solid-state method was

also applied to form $Li_{4-x}Ca_xTi_5O_{12}$ (with $x=0, 0.05, 0.075$ and 0.125). The characterisation of the $Li_4Ti_5O_{12}$ by XRD showed that the Ca dopant was successfully inserted into the $Li_4Ti_5O_{12}$ structure. As a result, it was found that Ca doping can improve performance at a high C level, and the best performance was shown by $Li_{3.85}Ca_{0.075}Ti_5O_{12}$ with a discharge capacity of $30.2 mAh/g$ at 12C, along with the increase of electronic conductivity and the decrease of particle size to shorten the diffusion distance [47]. Further analysis of $Li_4Ti_5O_{12}$ performance enhancement by doping was also carried out by [62], which pure $Li_4Ti_5O_{12}$ and Ge^{4+} doped $Li_4Ti_5O_{12}$ were successfully synthesised in the form of $Li_4Ge_xTi_{5-x}O_{12}$; $x = 0.1$ and 0.2 . Generally, germanium has intrinsic electrode properties such as charge carrier mobility and excellent lithium-ion diffusivity. Therefore, when it acts as a dopant, Ge can improve the electrochemical properties of $Li_4Ti_5O_{12}$ itself. Doping mechanisms generally use smaller amounts of dopant materials. In this study, Ge^{4+} doping was also carried out via solid state at $950^\circ C$ in the air for eight hours (with ethanol as solvent). The electrochemical characterisation results show that the doped $Li_4Ti_5O_{12}$ can increase its capacity compared to pure $Li_4Ti_5O_{12}$. The best doping composition results were obtained with $Li_4Ge_{0.1}Ti_{4.9}O_{12}$, with $x = 0.1$. The addition of germanium can effectively reduce the cell impedance and improve the diffusion of Li^+ ions, producing capacities of $159 mAh/g$ and $145 mAh/g$ at 0.1C and 1C, respectively, after 300 cycles.

On the other hand, Deng *et al.* synthesised Cu-doped anode-based $Li_4Ti_5O_{12}$ with a porous structure. The Cu-doped $Li_4Ti_5O_{12}$ was prepared via a facile synthesis-from-solution (DSS) route assisted by freeze-drying. The resulting Cu-doped $Li_4Ti_5O_{12}$ exhibited good cycling performance and rate capability, providing a stable capacity of $180.6 mAh/g$ at 10C and even after 500 cycles [67], and the study of Noerochim *et al.* showed that $Li_4Ti_5O_{12}$ doped with 0.2 mol iodide exhibited greatly improved lithium ion diffusion ability and ion conductivity compared to pure $Li_4Ti_5O_{12}$. It is due to the opening of larger pathways in the crystal structure of $Li_4Ti_5O_{12}$, and at the same time, it is found that lithium iodide-doped $Li_4Ti_5O_{12}$ has no significant effect on the size and shape of $Li_4Ti_5O_{12}$ particles [30].

Table 3. Electrochemical performance of different doping in $Li_4Ti_5O_{12}$ matrix

Doping species	Performance	Remarks	References
Nb^{5+}	$119.4 mAh/g$ at 5C with 500 cycles; $164.7 mAh/g$ at 1C after 200 cycles	Good capacity retention rate and cycle stability, especially at low temperature	[64], [65]
Lanthanum (La)	$164.7 mAh/g$ at 0.5C; $206.9 mAh/g$ at 1C after 100 cycles	Almost did not have the initial capacity loss; high rate capacity and cyclic, large-scale applications such as electric vehicles	[66], [67]
Iron (Fe)	$110 mAh/g$ at 1C; $100 - 125 mAh/g$; $192.1 mAh/g$ after 100 cycles	Good Li-ion insertion/extraction; high coulombic efficiency of approximately 100%	[68], [69], [70]
Sodium (Na)	$135 mAh/g$ at 5C after 200 cycles	Excellent cycling and safety	[71]
Bromine (Br)	$125 mAh/g$ at 1C; $133 mAh/g$ at 1C; $150.2 mAh/g$ at 1C after 50 cycles	Fast electronic and ion transmission, high-rate capability; higher cyclic stability than pristine $Li_4Ti_5O_{12}$	[72], [73], [74]

3.2.2. Non-metallic Doping

In this research, the modified doping effects of non-metallic elements (*F, Cl, Br, I, C, and N*) on $Li_4Ti_5O_{12}$ electrode materials have been explored respectively. It is found that each doping has different modification advantages. In terms of changes in $Li_4Ti_5O_{12}$ structure and in terms of changes in $Li_4Ti_5O_{12}$ electrochemical performance. Br dopants performed best in increasing the unit cell volume of $Li_4Ti_5O_{12}$ and resulted in greater capacity and rate performance of lithium titanate batteries than doped with *Cl* and *I* at 0.1C 164.5 mAh/g, 0.5C 162.3 mAh/g. On the other hand, *C* dopant significantly reduced the particle size and agglomeration between $Li_4Ti_5O_{12}$ particles, which made it capable of effectively reducing the charge transfer resistance compared with pure $Li_4Ti_5O_{12}$. Meanwhile, *N* dopants form an oxygen gap and a small amount of *TiN* metal structure, which can greatly improve the high-level performance of $Li_4Ti_5O_{12}$ (up to 4.1%) compared with pure $Li_4Ti_5O_{12}$. Meanwhile, doping with *F* also results in high capacity and rate performance of $Li_4Ti_5O_{12}$ batteries compared to doping with *Cl* and *I*. More details, the comparison of charge and discharge capacity, and cycling performances can be seen in Figure 3.

The overall results show that *C, N, and Br* dopants play an important role in improving the electrochemical performance of different $Li_4Ti_5O_{12}$. These three dopants can induce different Ti^{3+} active sites, narrow the band gap, and facilitate electron transport in the $Li_4Ti_5O_{12}$ grid. This research shows that in optimising the electrochemical performance of $Li_4Ti_5O_{12}$ it is very important to consider the properties of the material to be used such as the morphology, crystal structure, and electron structure of $Li_4Ti_5O_{12}$ that match the properties of non-metallic materials [76].

In another study, *N*-doped $Li_4Ti_5O_{12}$ was produced by thermal decomposition of $Li_4Ti_5O_{12}$ and melamine. As a result, surface modification of $Li_4Ti_5O_{12}$ (LTON12) with a certain change of *N* can improve the electronic conductivity and diffusivity of *Li* ions compared with pure $Li_4Ti_5O_{12}$. After 500 cycles in 5C, the *N*-doped sample yields a capacity of about 124 mAh/g with a high-capacity retention of 89.1%, while the undoped sample (pure $Li_4Ti_5O_{12}$) is about 43.7%. In fact, at 100C with a constant discharge rate of 1C, LTON12 still has a capacity of 74.3 mAh/g. This excellent electrochemical performance of *N*-doped $Li_4Ti_5O_{12}$ is attributed to the thin *TiN* layer on the particle surface [77].

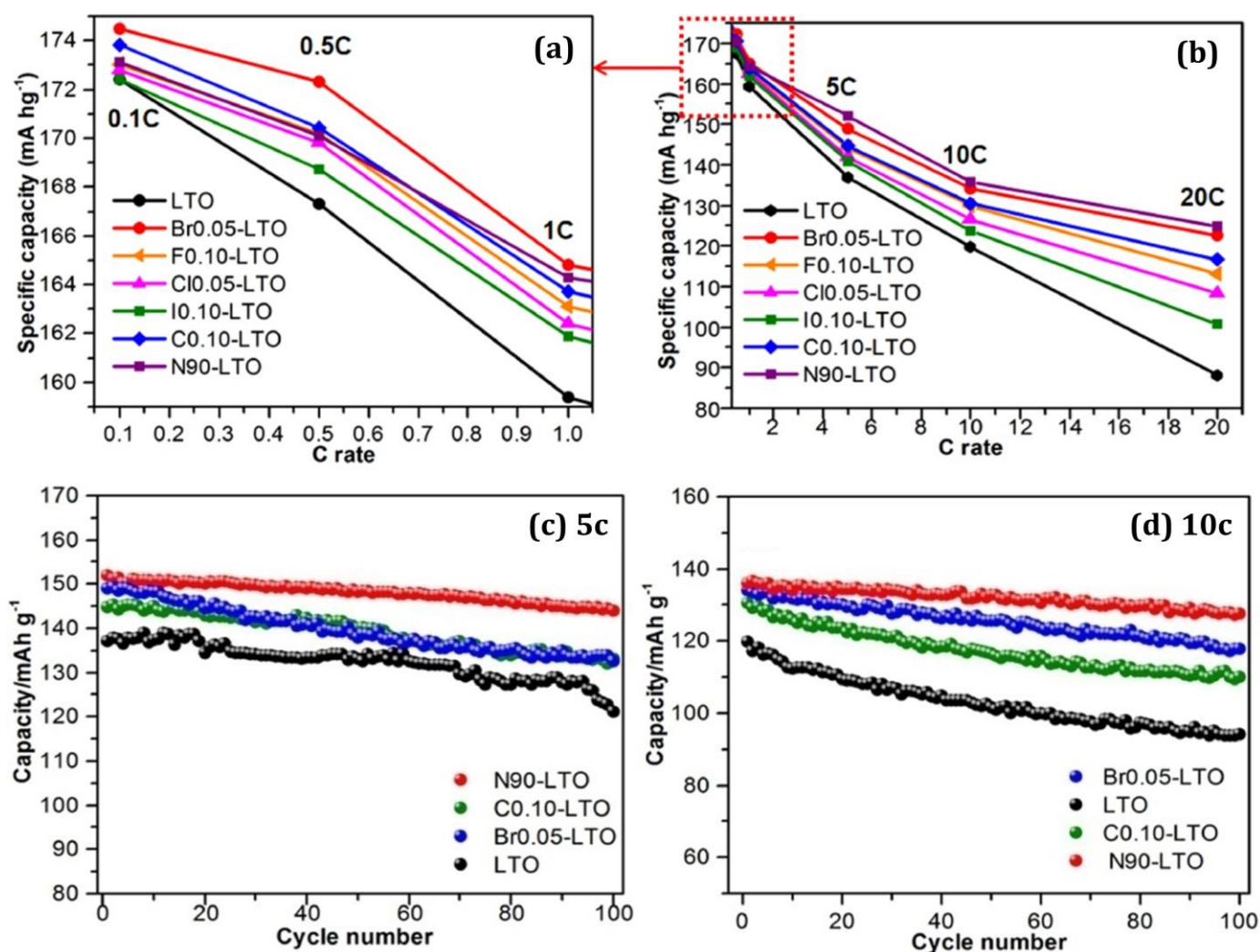


Figure 3. Comparison of charge and discharge capacity at (a) low rate (0.1C, 0.5C, 1C); (b) high rate (5C, 10C, 20C) and cycle performance at (c) 5C; (d) 10C [76]

3.2.3. Co-doping

The Al/Mn material was used to dope $Li_4Ti_5O_{12}$ and prepared by a solvent-thermal method. In this study, it was reported that the first cycle at 0.1C had a specific capacity of 240.1 mAh/g , and even after 100 cycles, the specific capacity only decreased by about 4.9% and still maintained a high capacity of 223.1 mAh/g . Furthermore, at different current levels from 0.5C to 7C, the specific capacities of $Li_4Ti_5O_{12}$ -Al/Mn were still high, ranging from 235.7 $mAhg^{-1}$ to 200.8 mAh/g . When the C-rate returned to 0.5C, the samples showed capacities between 200.8 mAh/g and 218.73 mAh/g . After the high C-rate cycle, the capacity decreased to only 14.8%. This means that even after many cycles the sample has successfully produced a high capacity. High-speed performance plays a key role in the charging and discharging rate, which is one of the most important electrochemical characteristics of Li-ion batteries. In addition, the high-speed stability of the cycling performance is essential for the fast charging and discharging process. This is attributed to the Li^+ migration in the two-phase phenomenon of $Li_4Ti_5O_{12}$, namely in $Li_4Ti_5O_{12}$ and $Li_7Ti_5O_{12}$ phases during the charge/discharge processes. This study also mentioned that $Li_4Ti_5O_{12}$ -Al/Mn has faster Li^+ insertion and extraction as well as better charge/discharge kinetics compared to other samples such as pure $Li_4Ti_5O_{12}$, $Li_4Ti_5O_{12}$ -Al and $Li_4Ti_5O_{12}$ -Mn. This is evident based on the characterisation, which shows that the Al and Mn doped CV curves are sharper and higher (**Figure 4** (a)) than the other samples [55].

Zhang *et al.* [78] also doped $Li_4Ti_5O_{12}$ by the sol-gel method from elemental materials such as Na^+ and Br^- to determine the effect of co-doping on the structure and electrochemical properties of $Li_4Ti_5O_{12}$ itself. It was found that codoping ($xNaBr - Li_4Ti_5O_{12}$, where $x = 0, 0.03, 0.04, 0.05$ and 0.06) was able to maintain the spinel crystal lattice by producing a more uniform phase and smaller particle size based on morphological and structural characterisation. The reduced particle size can be advantageous for effective electrolyte penetration. Each dopant has its own properties, including Na^+ dopants on Li sites, which can increase the lithium layer spacing and promote Li^+ migration. While the Br^- dopant on the O site is able to form covalent bonds with Ti and improve structural stability. In addition, with the addition of the Na/Br elements, this composite is able to provide an increase in high discharge capacity and is also able to reduce its current resistance value compared to no dopant/pure $Li_4Ti_5O_{12}$. The performance test is shown in **Figure 4** (b) using EIS characterisation. The test results show that Na/Br 0.05 has the lowest charge transfer resistance of about 151 Ω compared to other samples and has the best electrochemical performance of about 490.2 mAh/g and 243 mAh/g at 0.2C and 10C, respectively.

Zhang *et al.* described related EIS plots in which the semicircle in the high frequency region represents the material's charge transfer resistance, and the upright straight line in the low frequency region represents the diffusion of lithium ions in the electrode material [78]. However, the nyquist plots produced were seen to have skewed plots. This is probably due to the electrode surface

irregularity on the sample as mentioned by Hansika (2019) in [78].

Impurity dopants can be incorporated into the lithium titanate lattice to induce various effects on its performance as an anode material. By understanding the effects of impurity dopants, researchers can advance the development of high-performance $Li_4Ti_5O_{12}$ anode materials for next-generation lithium-ion batteries. Based on previous research, each dopant causes unique changes to the properties, structures, and performance of the respective material, thus allowing $Li_4Ti_5O_{12}$ to be customised to specific application needs, in particular to improve the conductivity, cyclability, and stability of $Li_4Ti_5O_{12}$ as an anode material for high performance lithium-ion battery applications. Therefore, it is very crucial to consider the properties and characteristics of each material to be used in doping $Li_4Ti_5O_{12}$.

4. MECHANISMS OF DOPANT EFFECT ON $Li_4Ti_5O_{12}$ ANODE PERFORMANCE

4.1. Authors Lattice Structure Changes

One of the main mechanisms that can affect the performance of Li-ion batteries on a doped anode is the occurrence of changes in lithium-ion diffusion kinetics or changes in lattice parameters within the anode material. Essentially, doping introduces foreign elements into the crystal lattice of the anode material, and this can have a significant impact on how lithium ions are transferred and stored during charge and discharge. Doping the anode material with impurity elements can introduce defects or voids within the crystal structure itself. These voids will provide additional sites or pathways for lithium-ion diffusion. Conversely, some dopants can disrupt the normal arrangement of atoms in the crystal lattice, creating an energy barrier that prevents the diffusion of lithium ions. These barriers can cause a delay in the movement of lithium ions, which can affect the battery's energy capacity. In addition, dopants that significantly change the electronic band structure of the anode material can affect the electrical and ionic conductivity, further affecting the flow kinetics of lithium-ion distribution. In addition, the concentration of dopants plays an important role in determining the effect of dopant concentration on anode performance. In the relationship between lattice strain and dopant concentration, low dopant concentrations can cause local changes that do not significantly affect the diffusion dynamics of lithium ions, while high concentrations can also cause significant changes, such as the overall lattice strain becoming larger over the entire region and showing a decrease in resistivity. In addition, changes in lattice parameters are also caused by the difference between the ionic radii of the two species (i.e., donor and acceptor), external pressure, and temperature variations. Suppose a dopant enters the lattice to be doped (e.g. $Li_4Ti_5O_{12}$ in this case), then the system becomes more distorted, which ultimately leads to the introduction of strain into the matrix and causes the induced lattice to undergo strain deformation [79], [80].

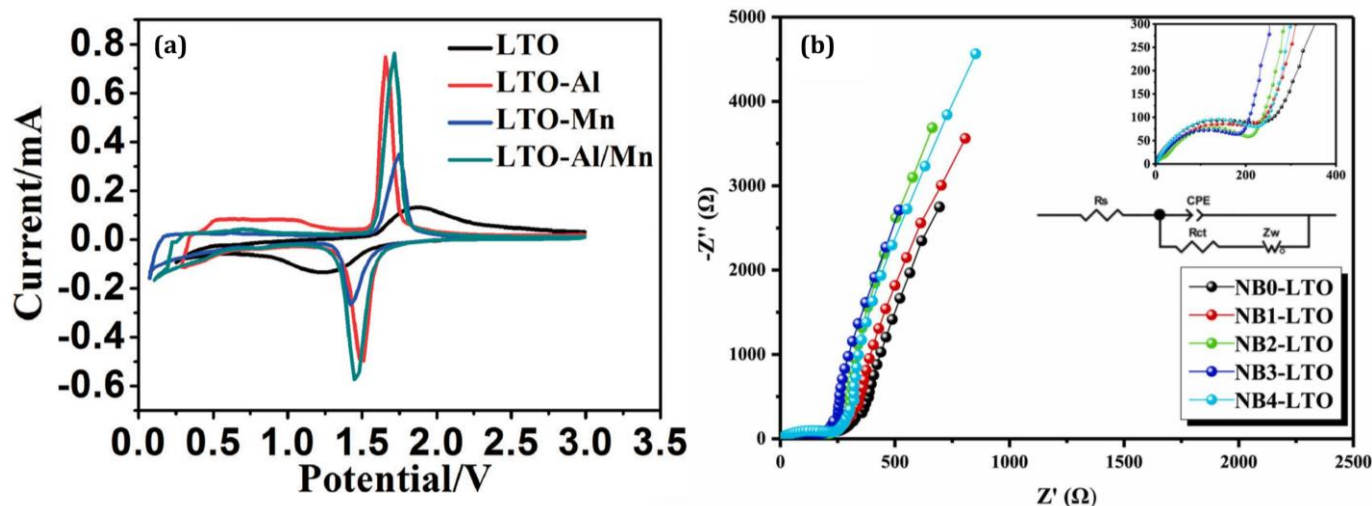


Figure 4. (a) Results of the comparison of the CV curves for pure LTO, LTO-Mn, LTO-Al and LTO-Al/Mn samples; (b) Comparative EIS characterisation results for pure LTO NB1-LTO, NB2-LTO, NB3-LTO and NB4-LTO [55], [78]

The effect of doping on the $Li_4Ti_5O_{12}$ lattice structure, particularly cobalt doping, is a complex and multifaceted phenomenon. It involves lattice expansion, changes in interatomic distances and phase transitions, all of which have a direct impact on the electrochemical performance of $Li_4Ti_5O_{12}$ as an anode for lithium-ion batteries. By tuning the lattice structure, doping can improve lithium-ion diffusion dynamics, electronic conductivity and ultimately the overall performance of $Li_4Ti_5O_{12}$ in lithium-ion batteries. Doping's multiple effects on the lattice structure highlight its importance for further development of energy storage technology [81].

In general, by providing different dopants into Li, Ti or O sites, it will provide an increase in the lattice parameters of the sample and be able to increase the concentration of lithium ion migration. Therefore, doping treatment can increase the spacing of the lithium layer, which is conducive to enhancing Li^+ migration, thereby reducing the free energy and obtaining higher lithium ion conductivity [78]. However, dopant ions can be doped simultaneously on Ti sites and Li sites at the 16d position, which may complicate the mechanism of doping effects in electrochemistry. Simultaneous substitution of Li^+ and Ti^{4+} by high-valence

cations will lead to excessive void formation. Although this may increase the lithium storage capacity of the battery, the excess lithium-occupied voids disrupt the "zero-strain" structure of $Li_4Ti_5O_{12}$ and reduce the cycle rate and performance of $Li_4Ti_5O_{12}$. Overall, each type of dopant has a positive effect on the electrochemical performance of $Li_4Ti_5O_{12}$ (as per the research presented above) [82].

As performed by Kim *et al.* in studying the effects of Zr^{4+} doping in $Li_4Ti_5O_{12}$ nanofibres on the lattice, electronic structure, and electrochemical properties of Li-ion batteries, it was found that the fibre dimensions and electronic structure upon Zr^{4+} doping in $Li_4Ti_5O_{12}$ lattice were almost unchanged. However, the given doping is able to increase the average lattice constant and diffusion coefficient of Li^+ . Based on Rietveld refinement, the estimated average lattice constant is about 8.360 Å for $Li_4Ti_5O_{12}$, and increases to 8.361 Å-8.362 Å for Zr-doped $Li_4Ti_5O_{12}$ (with illustration as shown in Figure 5). This increase is due to an increase in Li^+ diffusivity due to lattice distortion (expansion) as a result of Zr^{4+} doping rather than changes in the electronic structure affecting the electronic conductivity. By accommodating a small portion of Zr^{4+} ions on Ti^{4+} sites in the $Li_4Ti_5O_{12}$ lattice structure.

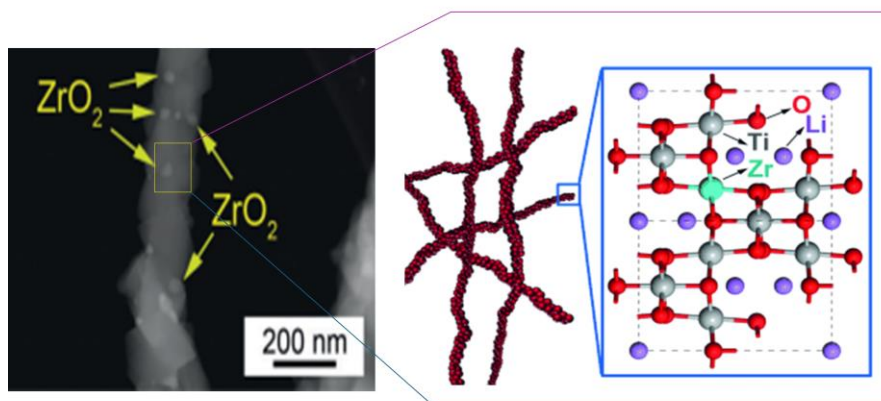


Figure 5. Illustration of lattice distortion in $Li_4Ti_5O_{12}$ 1D spinel nanostructure doped Zr^{4+} [83]

The lattice expansion of $Li_4Ti_5O_{12}$ through the substitution of Ti^{4+} with Zr^{4+} , an ion with a relatively large ionic radius, may have the benefit of facilitating and rapid intercalation/deintercalation of lithium ions during lithium-ion diffusion. These findings provide clear evidence that there is a relationship between structural changes and improved electrochemical performance caused by Zr^{4+} doping. As a result, $Li_4Ti_5O_{12}$ doped with Zr^{4+} is able to improve its electrochemical properties in the form of specific capacity, rate capability, and cycling properties when compared to undoped nanofibers [83].

4.2. Surface Effects and SEI Formation

In fact, stable SEI (solid electrolyte interface) formation initially plays an essential role in rechargeable batteries, protecting the anode from solvent decomposition at high negative voltages and enabling the design of batteries operating at high voltages beyond the "voltage window" for the electrochemical stability of the electrolyte. However, if SEI formation continues and is maintained during battery operation, it will become unstable and form a solid layer on the surface of the active material. This can lead to a continuous loss of lithium, rendering the Li-ion battery unusable. Thus, the formation of SEI at the electrode/electrolyte interface significantly affects the capacity and cycling stability of anode materials [84]. Dendrite growth results from the inhomogeneous precipitation and dissolution of Li metal, which is associated with the formation of an unstable SEI between the Li metal and the electrolyte [85]. As mentioned above, dendrite formation can cause significant thermal runaway in Li-ion batteries, making them unsafe [11].

The studies by Wang *et al.* found that electronic and ionic conductivity determine electrochemical performance and have a strong influence on dendrite growth. In these studies, it was mentioned that one way to suppress dendrite formation is to use electrolyte materials with high ionic conductivity so that only lithium-ion transfer takes place. Meanwhile, the electrical conductivity is recommended to be low/blank, with the purpose of having no electrons moving through the electrolyte liquid [86]. Furthermore, Goodenough & Kim have reviewed several types of electrolytes in Li batteries, namely electrolytes that meet the criteria of lithium-ion battery electrolytes, namely having an ionic conductivity above 10^{-1} mS/cm and a low viscosity [87]. Although $Li_4Ti_5O_{12}$ is a safe and stable anode, it unfortunately has a modest specific capacity value, and its use as an anode material requires the identification of a cathode with a better match. In this case, $LiFePO_4$ cathodes and $Li_4Ti_5O_{12}$ anodes have demonstrated safe and fast charging and discharging. Interestingly, in the research of Putra *et al.* they have successfully overcome the problem of SEI formation and rateability with a very simple method, namely modifying graphite anode material with Na- $Li_4Ti_5O_{12}$ composite through the addition of 4 wt% NaCl salt in the preparation process. In addition, Na- $Li_4Ti_5O_{12}$ -doped graphite can improve Li-ion kinetic diffusivity and stability with only 1 wt% Na- $Li_4Ti_5O_{12}$ composite. This is evidenced by the

high initial charge capacity test results at 0.1C of 356.69 mAh/g , and even a stable discharge capability of 264.64 mAh/g and 220.65 mAh/g at 0.2C and 1C respectively [88].

5. CONCLUSION

$Li_4Ti_5O_{12}$ is an alternative to graphite as an Li-ion batteries anode material due to its attractive properties such as zero strain, long cycle life, good thermal stability and ability to operate at extreme temperatures. $Li_4Ti_5O_{12}$ has brought significant progress and enormous potential in various applications (mobile phones, laptops, cameras, etc.). Recently, $Li_4Ti_5O_{12}$ has been explored for its application properties and use in high performance devices such as industrial equipment requiring safety, durability and fast charging for satellites and unmanned aerial vehicles (UAVs). Unfortunately, $Li_4Ti_5O_{12}$ is notorious for its low theoretical specific capacity (165 mAh/g). Therefore, in order to further improve performance and tailor properties for specific applications, impurity dopants have been investigated as a means of modifying the performance of $Li_4Ti_5O_{12}$. Throughout this review, it has been found that doping $Li_4Ti_5O_{12}$ can on average improve $Li_4Ti_5O_{12}$ performance (such as specific capacitance, rate capability, energy density, coulomb efficiency, and lifetime) compared to pure $Li_4Ti_5O_{12}$. Doping is one of the most effective ways to improve the functionality of $Li_4Ti_5O_{12}$ as an anode material with the best results. Each type of dopant causes unique changes to the material's properties, structure, and performance, allowing $Li_4Ti_5O_{12}$ to be tailored to specific application requirements. It is therefore very important to consider the properties and characteristics of each material to be used in doping $Li_4Ti_5O_{12}$. By modifying the lattice structure, doping can improve lithium-ion diffusion dynamics, electronic conductivity, and ultimately the overall performance of $Li_4Ti_5O_{12}$ in lithium-ion batteries. The different effects of doping on the lattice structure highlight the importance of doping for the further development of large-scale energy storage technologies.

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REFERENCES

- [1] Y. Chen *et al.*, "A review of lithium-ion battery safety concerns: The issues, strategies, and testing standards," *Journal of Energy Chemistry*, vol. 59, pp. 83–99, Aug. 2021, doi: 10.1016/j.jechem.2020.10.017.
- [2] "Handbook on Battery Energy Storage System," Manila, Philippines, Dec. 2018. doi: 10.22617/TCS189791-2.

- [3] K. Schmidt-Rohr, "How Batteries Store and Release Energy: Explaining Basic Electrochemistry," *Journal of Chemical Education*, vol. 95, no. 10, pp. 1801–1810, Oct. 2018, doi: 10.1021/acs.jchemed.8b00479.
- [4] T. Hordé, P. Achard, and R. Metkemeijer, "APACHE: Integrated Hybrid Fuel Cell System for 2-Seat All Electric Aircraft Propulsion," *28th Congress of the International Council of the Aeronautical Sciences 2012, ICAS 2012*, vol. 5, Sep. 2012.
- [5] F. Ahmed, F. Okoro, S. Amjad, E. Degasperri, and R. Da Silva, "Li-ion Batteries for Electric Mobility," Research Gate. [Online]. Available: https://www.researchgate.net/publication/331168520_Li-ion_Batteries_for_Electric_Mobility
- [6] O. Ramström, "Scientific Background on the Nobel Prize in Chemistry 2019 - Lithium-Ion Batteries," The Royal Swedish Academy of Sciences. [Online]. Available: <https://www.nobelprize.org/uploads/2019/10/advanced-chemistryprize2019.pdf>
- [7] H. Xia, Z. Luo, and J. Xie, "Nanostructured lithium titanate and lithium titanate/carbon nanocomposite as anode materials for advanced lithium-ion batteries," *Nanotechnology Reviews*, vol. 3, no. 2, Jan. 2014, doi: 10.1515/ntrev-2012-0049.
- [8] K. Sawai, Y. Iwakoshi, and T. Ohzuku, "Carbon materials for lithium-ion (shuttlecock) cells," *Solid State Ionics*, vol. 69, no. 3–4, pp. 273–283, Aug. 1994, doi: 10.1016/0167-2738(94)90416-2.
- [9] C. P. Sandhya, B. John, and C. Gouri, "Lithium titanate as anode material for lithium-ion cells: a review," *Ionics*, vol. 20, no. 5, pp. 601–620, May 2014, doi: 10.1007/s11581-014-1113-4.
- [10] M. G. Verde *et al.*, "Elucidating the Phase Transformation of Li₄Ti₅O₁₂ Lithiation at the Nanoscale," *ACS Nano*, vol. 10, no. 4, pp. 4312–4321, Apr. 2016, doi: 10.1021/acs.nano.5b07875.
- [11] S. Mahmud *et al.*, "Recent advances in lithium-ion battery materials for improved electrochemical performance: A review," *Results in Engineering*, vol. 15, p. 100472, Sep. 2022, doi: 10.1016/j.rineng.2022.100472.
- [12] X. Sun, P. V. Radovanovic, and B. Cui, "Advances in spinel Li₄Ti₅O₁₂ anode materials for lithium-ion batteries," *New Journal of Chemistry*, vol. 39, no. 1, pp. 38–63, 2015, doi: 10.1039/C4NJ01390E.
- [13] H. Zhang, Y. Yang, D. Ren, L. Wang, and X. He, "Graphite as anode materials: Fundamental mechanism, recent progress and advances," *Energy Storage Materials*, vol. 36, pp. 147–170, Apr. 2021, doi: 10.1016/j.ensm.2020.12.027.
- [14] I. Grobler, "Performance and Applications of Lithium Titanite Oxide Cells," Research Gate. [Online]. Available: https://www.researchgate.net/publication/364292551_Performance_and_Applications_of_Lithium_Titanite_Oxide_Cells
- [15] Z. Guo *et al.*, "Battery-Type Lithium-Ion Hybrid Capacitors: Current Status and Future Perspectives," *Batteries*, vol. 9, no. 2, p. 74, Jan. 2023, doi: 10.3390/batteries9020074.
- [16] K. Johnson *et al.*, "Synthesis, characterisation and electrochemical evaluation of lithium titanate anode for lithium ion cells," *Inorganic Chemistry Communications*, vol. 137, p. 109188, Mar. 2022, doi: 10.1016/j.inoche.2021.109188.
- [17] M. Vijayakumar *et al.*, "Lithium diffusion in Li₄Ti₅O₁₂ at high temperatures," *Journal of Power Sources*, vol. 196, no. 4, pp. 2211–2220, Feb. 2011, doi: 10.1016/j.jpowsour.2010.09.060.
- [18] K. M. Colbow, J. R. Dahn, and R. R. Haering, "Structure and electrochemistry of the spinel oxides LiTi₂O₄ and Li₄₃Ti₅₃O₄," *Journal of Power Sources*, vol. 26, no. 3–4, pp. 397–402, May 1989, doi: 10.1016/0378-7753(89)80152-1.
- [19] K. Amine *et al.*, "Nanostructured Anode Material for High-Power Battery System in Electric Vehicles," *Advanced Materials*, vol. 22, no. 28, pp. 3052–3057, Jul. 2010, doi: 10.1002/adma.201000441.
- [20] W. Zhang *et al.*, "Multi-Stage Structural Transformations in Zero-Strain Lithium Titanate Unveiled by in Situ X-ray Absorption Fingerprints," *Journal of the American Chemical Society*, vol. 139, no. 46, pp. 16591–16603, Nov. 2017, doi: 10.1021/jacs.7b07628.
- [21] L. Cheng, X.-L. Li, H.-J. Liu, H.-M. Xiong, P.-W. Zhang, and Y.-Y. Xia, "Carbon-Coated Li₄Ti₅O₁₂ as a High Rate Electrode Material for Li-Ion Intercalation," *Journal of The Electrochemical Society*, vol. 154, no. 7, p. A692, 2007, doi: 10.1149/1.2736644.
- [22] C. P. Sandhya, B. John, and C. Gouri, "Synthesis and electrochemical characterisation of electrospun lithium titanate ultrafine fibres," *Journal of Materials Science*, vol. 48, no. 17, pp. 5827–5832, Sep. 2013, doi: 10.1007/s10853-013-7375-9.
- [23] T. Ohzuku, A. Ueda, and N. Yamamoto, "Zero-Strain Insertion Material of Li [Li₁ / 3Ti₅ / 3] O₄ for Rechargeable Lithium Cells," *Journal of The Electrochemical Society*, vol. 142, no. 5, pp. 1431–1435, May 1995, doi: 10.1149/1.2048592.
- [24] H. Pourrahmani, C. M. I. Bernier, and J. Van herle, "The Application of Fuel-Cell and Battery Technologies in Unmanned Aerial Vehicles (UAVs): A Dynamic Study," *Batteries*, vol. 8, no. 7, p. 73, Jul. 2022, doi: 10.3390/batteries8070073.
- [25] M. Dev Anand, R. Sasidharakurup, T. . Mercy, T. M. Jacob, and S. Athula Devi, "Lithium-ion cells for space applications: Aspects of durability," *Advances in Space Research*, vol. 72, no. 7, pp. 2948–2958, Oct. 2023, doi: 10.1016/j.asr.2023.01.038.
- [26] J. Adamec, M. Danko, M. Taraba, and P. Drgona, "Analysis of selected energy storage for electric vehicle on the lithium based," *Transportation Research Procedia*, vol. 40, pp. 127–131, 2019, doi: 10.1016/j.trpro.2019.07.021.
- [27] H. Yan, D. Zhang, Qilu, X. Duo, and X. Sheng, "A review of spinel lithium titanate (Li₄Ti₅O₁₂) as electrode material for advanced energy storage devices,"

- Ceramics International*, vol. 47, no. 5, pp. 5870–5895, Mar. 2021, doi: 10.1016/j.ceramint.2020.10.241.
- [28] R. Liu, G. Ma, and H. Li, “Recent progress of lithium titanate as anode material for high performance Lithium-Ion batteries,” *Ferroelectrics*, vol. 580, no. 1, pp. 172–194, Aug. 2021, doi: 10.1080/00150193.2021.1905737.
- [29] C. Parthasarathy, H. Laaksonen, and P. Halagi, “Characterisation and Modelling Lithium Titanate Oxide Battery Cell by Equivalent Circuit Modelling Technique,” in *2021 IEEE PES Innovative Smart Grid Technologies - Asia (ISGT Asia)*, IEEE, Dec. 2021, pp. 1–5. doi: 10.1109/ISGTAsia49270.2021.9715566.
- [30] L. Noerochim, R. S. Prabowo, W. Widyastuti, D. Susanti, A. Subhan, and N. H. Idris, “Enhanced High-Rate Capability of Iodide-Doped Li₄Ti₅O₁₂ as an Anode for Lithium-Ion Batteries,” *Batteries*, vol. 9, no. 1, p. 38, Jan. 2023, doi: 10.3390/batteries9010038.
- [31] Y. Ha *et al.*, “Impact of Electrode Thickness and Temperature on the Rate Capability of Li₄Ti₅O₁₂/LiMn₂O₄ Cells,” *Journal of The Electrochemical Society*, vol. 168, no. 11, p. 110536, Nov. 2021, doi: 10.1149/1945-7111/ac3781.
- [32] J. Gao, C. Jiang, J. Ying, and C. Wan, “Preparation and characterization of high-density spherical Li₄Ti₅O₁₂ anode material for lithium secondary batteries,” *Journal of Power Sources*, vol. 155, no. 2, pp. 364–367, Apr. 2006, doi: 10.1016/j.jpowsour.2005.04.008.
- [33] R. Deng *et al.*, “Electrochemical performance of expanded graphite prepared from anthracite via a microwave method,” *Fuel Processing Technology*, vol. 227, p. 107100, Mar. 2022, doi: 10.1016/j.fuproc.2021.107100.
- [34] E. Yoo, J. Kim, E. Hosono, H. Zhou, T. Kudo, and I. Honma, “Large Reversible Li Storage of Graphene Nanosheet Families for Use in Rechargeable Lithium Ion Batteries,” *Nano Letters*, vol. 8, no. 8, pp. 2277–2282, Aug. 2008, doi: 10.1021/nl800957b.
- [35] G. Wang, X. Shen, J. Yao, and J. Park, “Graphene nanosheets for enhanced lithium storage in lithium ion batteries,” *Carbon*, vol. 47, no. 8, pp. 2049–2053, Jul. 2009, doi: 10.1016/j.carbon.2009.03.053.
- [36] R. Hu, W. Sun, Y. Chen, M. Zeng, and M. Zhu, “Silicon/graphene based nanocomposite anode: large-scale production and stable high capacity for lithium ion batteries,” *Journal of Materials Chemistry A*, vol. 2, no. 24, pp. 9118–9125, 2014, doi: 10.1039/C4TA01013B.
- [37] S. Thombare *et al.*, “Effect of electrolytes on the performance of graphene oxide anode material for ultracapacitor, Li-ion capacitor, and Li-ion battery: three-in-one approach,” *Indian Journal of Physics*, vol. 97, no. 10, pp. 2927–2942, Sep. 2023, doi: 10.1007/s12648-023-02647-6.
- [38] S. Cao, M. H. Tahmasebi, S. Gracious, J. C. Bennett, and M. N. Obrovac, “Preparation of Low Surface Area Si-Alloy Anodes for Li-Ion Cells by Ball Milling,” *Journal of The Electrochemical Society*, vol. 169, no. 6, p. 060540, Jun. 2022, doi: 10.1149/1945-7111/ac797e.
- [39] B. Wang, B. Luo, X. Li, and L. Zhi, “The dimensionality of Sn anodes in Li-ion batteries,” *Materials Today*, vol. 15, no. 12, pp. 544–552, Dec. 2012, doi: 10.1016/S1369-7021(13)70012-9.
- [40] Q. Zhu *et al.*, “Realizing a Rechargeable High-Performance Cu-Zn Battery by Adjusting the Solubility of Cu²⁺,” *Advanced Functional Materials*, vol. 29, no. 50, Dec. 2019, doi: 10.1002/adfm.201905979.
- [41] Z. Liu, Y. G. Andreev, A. Robert Armstrong, S. Brutti, Y. Ren, and P. G. Bruce, “Nanostructured TiO₂(B): the effect of size and shape on anode properties for Li-ion batteries,” *Progress in Natural Science: Materials International*, vol. 23, no. 3, pp. 235–244, Jun. 2013, doi: 10.1016/j.pnsc.2013.05.001.
- [42] S. Paul, M. A. Rahman, S. Bin Sharif, J.-H. Kim, S.-E.-T. Siddiqui, and M. A. M. Hossain, “TiO₂ as an Anode of High-Performance Lithium-Ion Batteries: A Comprehensive Review towards Practical Application,” *Nanomaterials*, vol. 12, no. 12, p. 2034, Jun. 2022, doi: 10.3390/nano12122034.
- [43] Y. Yu, J. L. Shui, and C. H. Chen, “Electrostatic spray deposition of spinel Li₄Ti₅O₁₂ thin films for rechargeable lithium batteries,” *Solid State Communications*, vol. 135, no. 8, pp. 485–489, Aug. 2005, doi: 10.1016/j.ssc.2005.05.045.
- [44] S.-W. Han, J. Jeong, and D.-H. Yoon, “Effects of high-energy milling on the solid-state synthesis of pure nano-sized Li₄Ti₅O₁₂ for high power lithium battery applications,” *Applied Physics A*, vol. 114, no. 3, pp. 925–930, Mar. 2014, doi: 10.1007/s00339-013-7768-2.
- [45] A. Salaam, A. Z. Syahrial, M. R. Nugraha, Faizah, A. Subhan, and B. Priyono, “Synthesis of lithium titanate/graphite-ZnO composites by solid-state method as anode material for lithium-ion batteries,” in *AIP Conference Proceedings 2232*, 2020, p. 030006. doi: 10.1063/5.0001714.
- [46] S.-W. Han, J.-W. Shin, and D.-H. Yoon, “Synthesis of pure nano-sized Li₄Ti₅O₁₂ powder via solid-state reaction using very fine grinding media,” *Ceramics International*, vol. 38, no. 8, pp. 6963–6968, Dec. 2012, doi: 10.1016/j.ceramint.2012.05.072.
- [47] B. Priyono, P. W. Winowatan, A. Z. Syahrial, Faizah, and A. Subhan, “Optimizing the performance of Li₄Ti₅O₁₂/LTO by addition of silicon microparticle in half cell lithium-ion battery anode,” *IOP Conference Series: Earth and Environmental Science*, vol. 105, p. 012121, Jan. 2018, doi: 10.1088/1755-1315/105/1/012121.
- [48] D. Mu *et al.*, “Nano-sized Li₄Ti₅O₁₂/C anode material with ultrafast charge/discharge capability for lithium ion batteries,” *Journal of Alloys and Compounds*, vol. 671, pp. 157–163, Jun. 2016, doi: 10.1016/j.jallcom.2016.02.095.
- [49] J. Zhang, H. Cao, X. Tang, W. Fan, G. Peng, and M. Qu, “Graphite/graphene oxide composite as high capacity and binder-free anode material for lithium ion batteries,” *Journal of Power Sources*, vol. 241, pp.

- 619–626, Nov. 2013, doi: 10.1016/j.jpowsour.2013.05.001.
- [50] Q. Wang, W. Liu, J. Zhang, X. Xie, and B. Xia, "Performance of electroless-plated lithium titanate/copper composites as anode materials in 18650-type lithium-ion batteries," *Journal of Solid State Electrochemistry*, vol. 19, no. 5, pp. 1411–1417, May 2015, doi: 10.1007/s10008-014-2734-2.
- [51] S. Sakai *et al.*, "Surface-Modified Li₄Ti₅O₁₂ in Highly Concentrated Aqueous Solutions for Use in Aqueous Rechargeable Lithium Batteries," *Journal of The Electrochemical Society*, vol. 167, no. 12, p. 120512, Aug. 2020, doi: 10.1149/1945-7111/ababd3.
- [52] B. Zhao, R. Ran, M. Liu, and Z. Shao, "A comprehensive review of Li₄Ti₅O₁₂-based electrodes for lithium-ion batteries: The latest advancements and future perspectives," *Materials Science and Engineering: R: Reports*, vol. 98, pp. 1–71, Dec. 2015, doi: 10.1016/j.mser.2015.10.001.
- [53] Z. N. Ezhyeh, M. Khodaei, and F. Torabi, "Review on doping strategy in Li₄Ti₅O₁₂ as an anode material for Lithium-ion batteries," *Ceramics International*, vol. 49, no. 5, pp. 7105–7141, Mar. 2023, doi: 10.1016/j.ceramint.2022.04.340.
- [54] Z. Lin, T. Liu, X. Ai, and C. Liang, "Publisher Correction: Aligning academia and industry for unified battery performance metrics," *Nature Communications*, vol. 10, no. 1, p. 328, Jan. 2019, doi: 10.1038/s41467-019-08321-y.
- [55] S. Zou *et al.*, "Electrochemical Characteristics of Pure and Al, Mn-doped Li₄Ti₅O₁₂ as High-performance Anode Materials for Li-ion Batteries," *Chemistry Letters*, vol. 48, no. 7, pp. 708–711, Jul. 2019, doi: 10.1246/cl.190154.
- [56] Y. Wu, X. Huang, L. Huang, and J. Chen, "Strategies for Rational Design of High-Power Lithium-ion Batteries," *Energy & Environmental Materials*, vol. 4, no. 1, pp. 19–45, Jan. 2021, doi: 10.1002/eem2.12088.
- [57] S. C. Maiti, M. A. Ghadkolai, R. K. Bordia, and C. Ghoroi, "Reaction kinetics to infer the effect of dopants on ion transport - A case study for Mo⁺⁶ doped lithium titanates (Li₂TiO₃- δ and Li₄Ti₅O₁₂- δ)," *Ceramics International*, vol. 44, no. 11, pp. 12580–12592, Aug. 2018, doi: 10.1016/j.ceramint.2018.04.055.
- [58] A. Balducci, D. Belanger, T. Brousse, J. W. Long, and W. Sugimoto, "Perspective—A Guideline for Reporting Performance Metrics with Electrochemical Capacitors: From Electrode Materials to Full Devices," *Journal of The Electrochemical Society*, vol. 164, no. 7, pp. A1487–A1488, May 2017, doi: 10.1149/2.0851707jes.
- [59] C. Xu, Z. Su, J. Wang, Z. Zhong, G. Zhu, and Y. Cao, "Liquid Metal Doped Li₄Ti₅O₁₂ as the Anode Material in Lithium-Ion Batteries for Temperature Tolerance Outdoor Secondary Equipment Power Supply," in *2019 4th International Conference on Power and Renewable Energy (ICPRE)*, IEEE, Sep. 2019, pp. 351–355. doi: 10.1109/ICPRE48497.2019.9034881.
- [60] J. Xiao *et al.*, "Understanding and applying coulombic efficiency in lithium metal batteries," *Nature Energy*, vol. 5, no. 8, pp. 561–568, Jun. 2020, doi: 10.1038/s41560-020-0648-z.
- [61] X. Deng, W. Li, M. Zhu, D. Xiong, and M. He, "Synthesis of Cu-doped Li₄Ti₅O₁₂ anode materials with a porous structure for advanced electrochemical energy storage: Lithium-ion batteries," *Solid State Ionics*, vol. 364, p. 115614, Jun. 2021, doi: 10.1016/j.ssi.2021.115614.
- [62] S. O. V., I. M. S., G. V. Alexander, and M. Ramaswamy, "Electrochemical characteristics of Ge incorporated Li₄Ti₅O₁₂ as an anode for Li-ion battery applications," *Materials Today Communications*, vol. 27, p. 102273, Jun. 2021, doi: 10.1016/j.mtcomm.2021.102273.
- [63] H.-J. Kim *et al.*, "A Comprehensive Review of Li-Ion Battery Materials and Their Recycling Techniques," *Electronics*, vol. 9, no. 7, p. 1161, Jul. 2020, doi: 10.3390/electronics9071161.
- [64] Q. Meng, F. Chen, Q. Hao, N. Li, and X. Sun, "Nb-doped Li₄Ti₅O₁₂-TiO₂ hierarchical microspheres as anode materials for high-performance Li-ion batteries at low temperature," *Journal of Alloys and Compounds*, vol. 885, p. 160842, Dec. 2021, doi: 10.1016/j.jallcom.2021.160842.
- [65] L. Shi, X. Hu, and Y. Huang, "Fast microwave-assisted synthesis of Nb-doped Li₄Ti₅O₁₂ for high-rate lithium-ion batteries," *Journal of Nanoparticle Research*, vol. 16, no. 4, p. 2332, Apr. 2014, doi: 10.1007/s11051-014-2332-3.
- [66] D. Wang, C. Zhang, Y. Zhang, J. Wang, and D. He, "Synthesis and electrochemical properties of La-doped Li₄Ti₅O₁₂ as anode material for Li-ion battery," *Ceramics International*, vol. 39, no. 5, pp. 5145–5149, Jul. 2013, doi: 10.1016/j.ceramint.2012.12.010.
- [67] T.-F. Yi *et al.*, "High rate cycling performance of lanthanum-modified Li₄Ti₅O₁₂ anode materials for lithium-ion batteries," *Journal of Power Sources*, vol. 214, pp. 220–226, Sep. 2012, doi: 10.1016/j.jpowsour.2012.04.101.
- [68] R. A. Hernández-Carrillo, G. Ramos-Sánchez, G. Guzmán-González, N. A. García-Gomez, I. González, and E. M. Sanchez-Cervantes, "Synthesis and characterization of iron - doped Li₄Ti₅O₁₂ microspheres as anode for lithium-ion batteries," *Journal of Alloys and Compounds*, vol. 735, pp. 1871–1877, Feb. 2018, doi: 10.1016/j.jallcom.2017.11.218.
- [69] I. A. Stenina *et al.*, "Influence of iron doping on structure and electrochemical properties of Li₄Ti₅O₁₂," *Electrochimica Acta*, vol. 219, pp. 524–530, Nov. 2016, doi: 10.1016/j.electacta.2016.10.034.
- [70] J.-R. Kang, G.-X. Dong, Z.-F. Li, and L. Li, "Enhanced electrochemical performance of Fe-doping Li₄Ti₅O₁₂ anode material for energy storage device," *Chemical Papers*, vol. 74, no. 5, pp. 1495–

- 1504, May 2020, doi: 10.1007/s11696-019-01002-6.
- [71] T.-F. Yi, S.-Y. Yang, X.-Y. Li, J.-H. Yao, Y.-R. Zhu, and R.-S. Zhu, "Sub-micrometric $\text{Li}_{4-x}\text{Na}_x\text{Ti}_5\text{O}_{12}$ ($0 \leq x \leq 0.2$) spinel as anode material exhibiting high rate capability," *Journal of Power Sources*, vol. 246, pp. 505–511, Jan. 2014, doi: 10.1016/j.jpowsour.2013.08.005.
- [72] J. B. Kim, S. G. Lee, S.-Y. Choi, J. Kim, and S. O. Kim, "Doping behavior of Br in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode materials and their electrochemical performance for Li-ion batteries," *Ceramics International*, vol. 45, no. 14, pp. 17574–17579, Oct. 2019, doi: 10.1016/j.ceramint.2019.05.322.
- [73] J. Wang, S. Zhao, J. Xie, D. Ruan, and F. Zhao, "Enhanced high-rate performance of Br-doping $\text{Li}_4\text{Ti}_5\text{O}_{12}$ microspheres as anode materials for lithium-ion batteries," *Journal of Solid State Chemistry*, vol. 303, p. 122479, Nov. 2021, doi: 10.1016/j.jssc.2021.122479.
- [74] Y. Qi, Y. Huang, D. Jia, S.-J. Bao, and Z. P. Guo, "Preparation and characterization of novel spinel $\text{Li}_4\text{Ti}_5\text{O}_{12-x}\text{Br}_x$ anode materials," *Electrochimica Acta*, vol. 54, no. 21, pp. 4772–4776, Aug. 2009, doi: 10.1016/j.electacta.2009.04.010.
- [75] F. Li, M. Zeng, J. Li, and H. Xu, "Short Communication: Preparation and Electrochemical Performance of Mg-doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Nanoparticles as Anode Materials for Lithium-Ion Batteries," *International Journal of Electrochemical Science*, vol. 10, no. 12, pp. 10445–10453, Dec. 2015, doi: 10.1016/S1452-3981(23)11270-3.
- [76] Y. Li, H. Gao, and W. Yang, "Enhancements of the structures and electrochemical performances of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrodes by doping with non-metallic elements," *Electrochimica Acta*, vol. 409, p. 139993, Mar. 2022, doi: 10.1016/j.electacta.2022.139993.
- [77] M. Guo, S. Wang, L.-X. Ding, L. Zheng, and H. Wang, "Synthesis of novel nitrogen-doped lithium titanate with ultra-high rate capability using melamine as a solid nitrogen source," *Journal of Materials Chemistry A*, vol. 3, no. 20, pp. 10753–10759, 2015, doi: 10.1039/C5TA01179E.
- [78] L. Zhang, J. Zhang, and B. Xu, "Enhancing the electrochemical performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode materials by codoping with Na and Br," *Journal of Alloys and Compounds*, vol. 903, p. 163962, May 2022, doi: 10.1016/j.jallcom.2022.163962.
- [79] T. Ailiumaer, Y. Yang, J. Guo, B. Raghathamachar, and M. Dudley, "Studies on Lattice Strain Variation due to Nitrogen Doping by Synchrotron X-ray Contour Mapping Technique in PVT-Grown 4H-SiC Crystals," *Journal of Electronic Materials*, vol. 48, no. 5, pp. 3363–3369, May 2019, doi: 10.1007/s11664-019-07077-x.
- [80] P. Kaur *et al.*, "Correlation among lattice strain, defect formation and luminescence properties of transition metal doped ZnO nano-crystals prepared via low temperature technique," *Materials Research Express*, vol. 6, no. 11, p. 115920, Oct. 2019, doi: 10.1088/2053-1591/ab4752.
- [81] H. S. Bhatti, S. Jabeen, A. Mumtaz, G. Ali, S. Qaisar, and S. Hussain, "Effects of cobalt doping on structural, optical, electrical and electrochemical properties of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode," *Journal of Alloys and Compounds*, vol. 890, p. 161691, Jan. 2022, doi: 10.1016/j.jallcom.2021.161691.
- [82] C. Han *et al.*, "Large Polarization of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Lithiated to 0 V at Large Charge/Discharge Rates," *ACS Applied Materials & Interfaces*, vol. 8, no. 29, pp. 18788–18796, Jul. 2016, doi: 10.1021/acsami.6b04239.
- [83] J. Kim *et al.*, "Zr⁴⁺ Doping in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Anode for Lithium-Ion Batteries: Open Li + Diffusion Paths through Structural Imperfection," *ChemSusChem*, vol. 7, no. 5, pp. 1451–1457, May 2014, doi: 10.1002/cssc.201301393.
- [84] M. B. Pinson and M. Z. Bazant, "Theory of SEI Formation in Rechargeable Batteries: Capacity Fade, Accelerated Aging and Lifetime Prediction," *Journal of The Electrochemical Society*, vol. 160, no. 2, pp. A243–A250, 2013, doi: 10.1149/2.044302jes.
- [85] D. Cao, X. Sun, Q. Li, A. Natan, P. Xiang, and H. Zhu, "Lithium Dendrite in All-Solid-State Batteries: Growth Mechanisms, Suppression Strategies, and Characterizations," *Matter*, vol. 3, no. 1, pp. 57–94, Jul. 2020, doi: 10.1016/j.matt.2020.03.015.
- [86] S. Wang, M. Yan, Y. Li, C. Vinado, and J. Yang, "Separating electronic and ionic conductivity in mixed-conducting layered lithium transition-metal oxides," *Journal of Power Sources*, vol. 393, pp. 75–82, Jul. 2018, doi: 10.1016/j.jpowsour.2018.05.005.
- [87] J. B. Goodenough and Y. Kim, "Challenges for Rechargeable Li Batteries," *Chemistry of Materials*, vol. 22, no. 3, pp. 587–603, Feb. 2010, doi: 10.1021/cm901452z.
- [88] M. I. Putra, S. U. Muzayanha, Y. Rizal, Fadilah, H. Widiyandari, and A. Purwanto, "Synthesis of Modified Graphite with High Crystalline Na-LTO by Simple Doping Method," *IOP Conference Series: Materials Science and Engineering*, vol. 1096, no. 1, p. 012143, Mar. 2021, doi: 10.1088/1757-899X/1096/1/012143.