


# LTO as a promising anode material for aqueous batteries: Synthesis routes, properties, and electrode preparation approaches.

Pigounakis Emmanouil

Department of Electrical and Computer Engineering

Hellenic Mediterranean University

M.Sc. Nanotechnology for Energy Applications

Heraklion, Crete, 2026

# Acknowledgements

I would like to express my sincere gratitude to my supervisor, Prof. Vernardou Dimitra, for her valuable guidance, constructive feedback, and continuous support throughout the development of this thesis. Her scientific insight and encouragement were essential for the completion of this work.

I am also deeply grateful to PhD candidate Apostolopoulou Maria, whose guidance, thoughtful comments, and careful corrections greatly contributed to improving both the clarity and quality of this thesis.

I am especially grateful to my wife, with whom I had the privilege of sharing this postgraduate journey. Participating together in the same program made this experience even more meaningful and motivating.

My deepest appreciation goes to our two children, whose presence and love constantly reminded me of the importance of perseverance and dedication.

Finally, I would like to express my deepest gratitude to everyone who supported me throughout this academic journey and contributed, directly or indirectly, to the completion of this thesis.

# Abstract

The growing integration of renewable energy sources into modern electricity systems has significantly increased the need for energy-storage technologies that are safe, sustainable, and cost-effective. Among the various alternatives under investigation, aqueous lithium-ion batteries (ALIBs) have emerged as a promising option due to their intrinsic safety, high ionic conductivity, environmental compatibility, and the use of non-flammable electrolytes. Nevertheless, their broader deployment remains constrained by the narrow electrochemical stability window of water and by the complex interfacial reactions occurring at the electrode–electrolyte interface.

Lithium titanate ($Li_4Ti_5O_{12}$, LTO) has attracted considerable attention as an anode material for aqueous systems because of its exceptional structural stability, negligible volume change during lithiation and delithiation, and relatively high operating potential, which helps mitigate hydrogen evolution. This thesis presents a comprehensive literature-based study of LTO in ALIB configurations, examining synthesis approaches, structural and electrochemical characteristics, electrolyte design strategies, and electrode fabrication techniques.

Particular attention is devoted to the influence of electrolyte chemistry on the electrochemical stability window and the interfacial processes governing battery performance. Conventional dilute aqueous electrolytes are evaluated alongside advanced electrolyte systems, including water-in-salt electrolytes, gel-polymer electrolytes, and localized high-concentration electrolytes, all of which aim to expand the operational voltage window and improve interfacial stability. In parallel, electrode fabrication methods such as spray deposition and tape casting are critically analyzed with respect to their effects on coating uniformity, adhesion, thickness control, and scalability.

Overall, this study demonstrates that the performance and durability of ALIBs depend not only on the intrinsic properties of the electrode materials but also on the synergistic interaction between electrolyte composition, electrode architecture, and fabrication methodology. By integrating these aspects, this work provides a systematic overview of current challenges and outlines potential directions for the development of stable and efficient LTO-based ALIB systems.

**Keywords:** Aqueous lithium-ion batteries, LTO, Electrode fabrication, Electrolyte engineering, WISE, Interfacial stability, energy storage systems.

# Table of Contents

**Acknowledgements** ..... 1

**Abstract** ..... 2

**Table of Contents** ..... 3

**List of Figures** ..... 5

**List of Tables** ..... 7

**1. Introduction** ..... 8

*1.1 The Need for Energy Storage and the Emergence of Aqueous Systems* ..... 8

*1.2 Operating Principle of ALIBs* ..... 12

*1.3 Anodes Used in Aqueous Systems* ..... 15

*1.4 Electrolytes for Aqueous Systems* ..... 20

*1.5 Limitations of Anodes in Aqueous Systems* ..... 25

1.5.1 Interfacial Instability and Hydrogen Evolution ..... 26

1.5.2 Chemical Dissolution and Surface Degradation ..... 27

1.5.3 Surface Engineering Strategies ..... 27

1.5.4 Bulk Doping and Lattice Engineering ..... 28

*1.6 Summary* ..... 29

***1.7 References*** ..... 30

**2. Structural and Electrochemical Characteristics of LTO Anodes** ..... 32

*2.1 Structure and Characteristics of Lithium Titanate* ..... 32

*2.2 Comparison with other Anodes* ..... 36

*2.3 Enhancing LTO Stability* ..... 39

***2.4 References*** ..... 4242

**3. Synthesis Methods of LTO** ..... 4545

*3.1 Purpose of the Synthesis* ..... 4545

*3.2 Synthesis Methods* ..... 4646

3.2.1 Sol–gel synthesis ..... 4646

3.2.2 Hydrothermal synthesis ..... 48

3.2.3 Solid-state synthesis ..... 4848

*3.3 Synthesis Comparison* ..... 49

***3.4 References*** ..... 5050

**4. Fabrication and Immobilization of LTO Electrode** ..... 5151

*4.1 Importance of Uniformity and Adhesion* ..... 5151

*4.2 Spray Deposition Technique* ..... *53*
4.2.1 Principle of Spray Deposition ..... 54
4.2.2 Microstructural Uniformity ..... 5454
4.2.3 Thickness Control ..... 56
4.2.4 Drying Dynamics and Adhesion ..... 5656
4.2.5 Process Parameters and Polyparametric Nature ..... 5757
4.2.6 Dispersion versus Slurry Considerations in Aqueous Spray Processing ..... 5858
4.2.7 Summary ..... 59
*4.3 Tape Casting (Doctor-Blade) Technique* ..... *60*
*4.4 Comparative Evaluation of Spray Deposition and Tape Casting* ..... *63*
***4.5 References*** ..... *67*
**5. Discussion – Overall Review ..... 69**
*5.1 Summary of Key Findings* ..... *69*
*5.2 Critical Assessment of Electrode Fabrication Techniques* ..... *69*
*5.3 Interplay Between Material Properties, Electrolyte Chemistry, and Electrode Architecture* ..... *70*
*5.4 Identification of Research Gaps* ..... *71*
**6. Perspectives ..... 71**
*6.1 Future Experimental Design* ..... *71*
*6.2 Exploration of Advanced Electrolyte Concepts* ..... *72*
*6.3 Toward LTO/LMO Aqueous Full Cells* ..... *72*
*6.4 Outlook* ..... *73*

# List of Figures

**Figure 1.1:** Schematic comparison between organic (non-aqueous) and aqueous electrolytes in LIBs, illustrating differences in safety, electrochemical stability window, cost, and ionic conductivity. Conceptual illustration based on literature reports [4, 5, 8]. .....9
**Figure 1.2:** (A) Complex LiTFSI-dependent cathodic behavior at the Al anode, (B) anodic behavior at a Ti cathode, (C) WiSE electrochemical stability window, and (D) the charge/discharge behavior of the $Mo_6S_8$ anode and $LiMn_2O_4$ cathode with WiSE. Reproduced from [12]. .....10
**Figure 1.3:** Schematic illustration of a LIB during discharge/charge showing coupled ionic and electronic transport processes. Conceptual illustration based on LIB operating principles described in the literature [2, 10]. .....14
**Figure 1.4:** Crystal structure of spinel $Li_4Ti_5O_{12}$. Lithium ions occupy the tetrahedral 8a sites, while the octahedral 16d sites are shared by $Ti^{4+}$ and a fraction of $Li^+$ ions ($Li_{1/6}Ti_{5/6}$). In the related spinel $LiTi_2O_4$, the 16d sites are occupied by mixed-valence $Ti^{3.5+}$. Adopted from Ohzuku et al. [14]. .....17
**Figure 2.1:** Schematic representation of the lithiation and delithiation mechanism in spinel $Li_4Ti_5O_{12}$, illustrating lithium insertion into octahedral sites while preserving the oxygen framework and maintaining minimal lattice distortion. Adapted from Wagemaker et al. [5]. .....32
**Figure 2.2:** Schematic representation of competing electrochemical reactions at the anode–electrolyte interface in aqueous battery systems, highlighting the competition between $Li^+$ insertion and hydrogen evolution reactions (HER). Adapted from Liu et al. [14]. .....33
**Figure 2.3:** Overview of electrolyte engineering strategies for aqueous electrochemical energy storage systems, including dilute and concentrated aqueous electrolytes, water-in-salt electrolytes, and deep eutectic solvent systems. These approaches modify ion solvation structures and reduce the activity of free water molecules, thereby extending the electrochemical stability window of aqueous batteries [38-41].....35
**Figure 2.4:** Comparison of $Li^+$ solvation structures in dilute aqueous electrolytes and water-in-salt electrolytes, illustrating the reduction of free water molecules and the formation of an anion-rich solvation environment at high salt concentrations. Adapted from Suo et al. [8]. .....35
**Figure 2.5:** Representative operando spectroelectrochemical cell configurations used for in-situ investigation of battery electrodes. (A) Electrochemical cell designed for operando Raman spectroscopy, where a laser beam probes the working electrode during electrochemical cycling. (B) Exploded view of an operando spectroelectrochemical cell enabling optical access through a borosilicate window. (C) Cross-section of an operando cell used for laser-based characterization of electrode processes. These configurations allow real-time monitoring of interfacial reactions such as gas evolution

and surface chemistry changes during battery operation. Adapted from operando battery spectroscopy studies [32,33,45]. ..... 40
**Figure 2.6:** Conceptual representation of electrochemical operation in polymer-based electrolyte systems. The electrode is immersed in an electrolyte environment in which ion transport occurs through a polymer-confined electrolyte phase. The polymer network spatially restricts solvent mobility while maintaining ionic conductivity, thereby stabilizing the electrode–electrolyte interface and reducing parasitic reactions such as hydrogen evolution. Adapted from recent studies on gel polymer electrolytes for rechargeable batteries [38–41]. ..... 41
**Figure 3.1:** Schematic illustration of the sol–gel synthesis process. Adapted from Wang et al. [5] ..... 48
**Figure 4.1:** Schematic diagram of the spray coating process, shown at two different times of a spray pass. Adopted from Lee et al. [6] ..... 54
**Figure 4.2:** Schematic diagrams of the electrodes with coating defects. (a) Slurry phase of coating; (b) components sedimentation; (c) delamination of coating from current collector; (d) coating cracking and delamination; (e) components segregation; (f) desirable dried electrode coating with homogenous distribution of components. Adapted from Zhang et al. [4]..... 55
**Figure 4.3:** Schematic illustration of binder migration during the drying of lithium-ion battery electrodes. Solvent evaporation induces convective flow within the coating layer, which can transport binder toward the surface and generate concentration gradients across the electrode thickness. Adapted from Zihrul et al., Batteries [14]). 57
**Figure 4.4:** Schematic representation of the drying process in lithium-ion battery electrodes and the resulting electrode microstructure after film solidification. Solvent evaporation from the coating surface induces convective transport within the slurry layer, redistributing binder and conductive additives and influencing the final electrode microstructure. Adapted from Jaiser et al. [15]. ..... 61
**Figure 4.5:** Experimental analysis of binder distribution in lithium-ion battery electrodes under different drying conditions. Increasing drying rates promote binder accumulation near the electrode surface and depletion near the current collector interface, leading to structural gradients that can affect adhesion and transport properties. Adapted from Jaiser et al. [15]..... 62
**Figure 4.6:** Schematic illustration of electrode fabrication methods showing (a) spray coating and (b) tape casting processes. Adopted from Font et al. [2]..... 64

# List of Tables

**Table 1.1:** Comparison of representative organic and aqueous LIB systems.....12
**Table 1.2:** Comparative overview of representative anode materials investigated for ALIBs, highlighting the trade-off between theoretical capacity and electrochemical stability in water.....19
**Table 1.3:** Comparison of the physicochemical and electrochemical properties of typical aqueous electrolytes used in ALIBs.....21
**Table 1.4:** Comparison of electrolyte engineering strategies in LIBs.....24
**Table 2.1:** Comparison of representative negative-electrode materials for aqueous lithium-ion batteries (ALIBs) under HER-limited conditions.....38
**Table 3.1:** Comparison of major $Li_4Ti_5O_{12}$ synthesis routes and their implications for electrochemical applications.....49
**Table 4.1:** Comparative summary of spray deposition and tape casting techniques for LTO-based aqueous anodes, highlighting trade-offs in thickness control, uniformity, adhesion, formulation sensitivity, and scalability.....65

# 1. Introduction

## 1.1 The Need for Energy Storage and the Emergence of Aqueous Systems

The global transition toward energy decarbonization has profoundly transformed electricity generation. As a result, electricity systems increasingly rely on renewable energy sources such as solar photovoltaics and wind power. Although these technologies enable electricity production with minimal carbon emissions, their power output is inherently intermittent and strongly dependent on weather conditions. This intermittency creates temporal mismatches between energy supply and demand, resulting in renewable-energy curtailment during low-demand periods and grid instability during peak demand. Consequently, the deployment of large-scale, efficient, and safe energy storage systems has become one of the most critical technological and economic challenges for modern power grids [1, 2].

Among the available energy storage technologies—including pumped hydroelectric storage, compressed air energy storage, flywheels, supercapacitors, and hydrogen-based systems—electrochemical batteries play a central role due to their high round-trip efficiency, modularity, scalability, and fast response time [2]. Since their commercialization in 1991, lithium-ion batteries (LIBs) have dominated a broad spectrum of applications ranging from portable electronic devices and consumer electronics to electric mobility and stationary energy-storage systems supporting renewable integration and grid stabilization [2, 3]. In particular, portable electronics remain one of the most mature and technologically demanding application domains, where requirements such as long cycle life, fast charging capability, operational safety, and power reliability have driven the development of electrodes, including lithium titanate ($Li_4Ti_5O_{12}$, LTO)-based systems. Conventional LIBs operate via the reversible intercalation of $Li^+$ ions into the crystalline electrode host structures, enabling high operating voltages (>3.7 V), gravimetric energy densities exceeding 250 Wh $kg^{-1}$, volumetric energy densities above 600 Wh $L^{-1}$, and long cycle life [2, 3].

Despite their technological maturity, conventional LIBs face increasing concerns related to safety, cost, and environmental sustainability [4]. Commercial electrolytes typically consist of $LiPF_6$ dissolved in organic carbonate solvents such as ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC), which are volatile, flammable, and thermally unstable [4]. Under abuse conditions—including overcharging, internal short circuits, or mechanical damage—electrolyte decomposition may initiate thermal runaway processes that lead to fire or explosion hazards [5]. Mitigation strategies therefore require complex battery management systems, flame-retardant components, and active thermal regulation, increasing manufacturing cost and system complexity while potentially reducing long-term reliability [5]. At the same time, the extraction and processing of transition metals used

in high-energy cathodes, such as $LiCoO_2$ and Ni-rich layered oxides, raise environmental and sustainability concerns, while recycling of organic electrolytes remains energy intensive and technically challenging [6, 7]. Leakage or improper disposal of organic solvents further introduces environmental risks [6, 7]. These combined limitations have intensified research toward alternative battery chemistries that are intrinsically safer, environmentally benign, and economically sustainable—particularly for applications where durability, safety, and operational stability outweigh maximum energy density requirements [8].

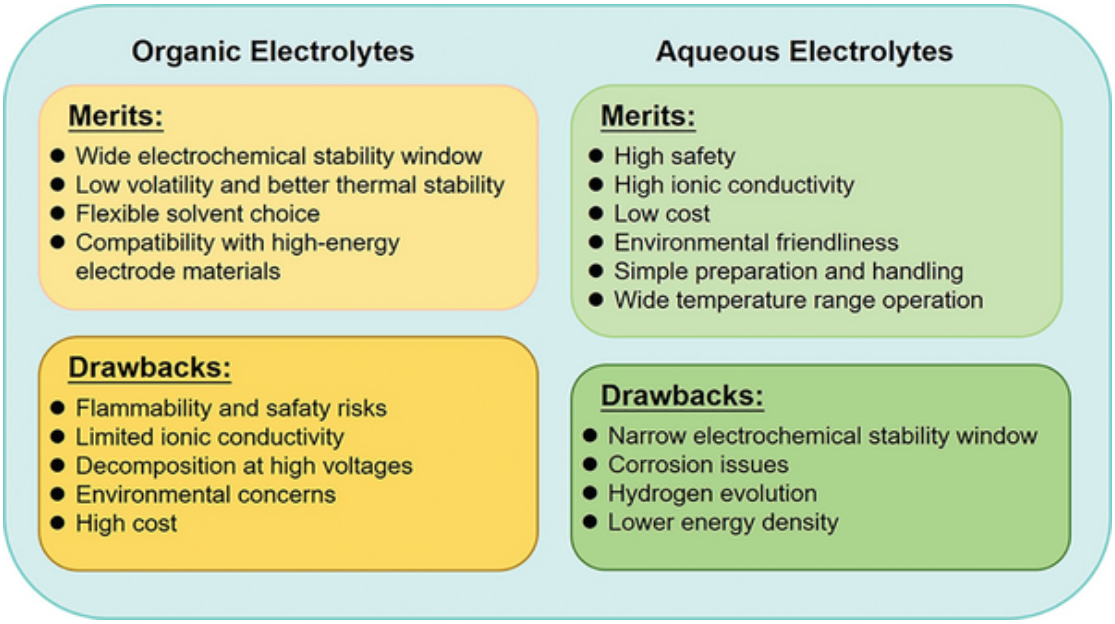



***Figure 1.1111:*** *Schematic comparison between organic (non-aqueous) and aqueous electrolytes in LIBs, illustrating differences in safety, electrochemical stability window, cost, and ionic conductivity. Conceptual illustration based on literature reports [4, 5, 8].*

Figure 1.1 shows the fundamental differences between conventional organic-electrolyte LIBs and emerging aqueous systems [4, 5, 8]. Organic electrolytes provide a wide electrochemical stability window and compatibility with high-energy electrode materials, but suffer from flammability, limited ionic conductivity, high cost, and environmental concerns [4, 5]. In contrast, aqueous electrolytes offer intrinsic safety, higher ionic conductivity, low cost, environmental friendliness, and simpler handling, albeit at the expense of a narrower electrochemical stability window and lower achievable energy density [8, 9].

This trade-off has renewed interest in ALIBs as intrinsically safer alternatives [10]. In aqueous electrolytes, water replaces organic solvents, offering a high dielectric constant ($\varepsilon \approx 78$ at 25 °C) [11] , which promotes strong salt dissociation and results in ionic conductivities typically in the range of $10^{-2}$–$10^{-3}$ $S \cdot cm^{-1}$—approximately one order of magnitude higher than those of organic electrolytes [10]. In addition, water is non-flammable, abundant, inexpensive, and exhibits a high specific heat capacity (~4.18 J $g^{-1}$ $K^{-1}$), which favors effective thermal management and operational safety [10]. These properties make aqueous systems particularly attractive for grid-scale storage,

microgrids, and community energy-storage applications, where safety and cost are prioritized over maximum energy density [2, 10].

However, the electrochemical stability window of water is thermodynamically limited by the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER), which define the lower and upper potential boundaries of aqueous electrolytes, respectively [9, 10, 12, 14]:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-(E^\circ = 0 \text{ V vs SHE}) \quad (1)$$
$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-(E^\circ = 1.23 \text{ V vs SHE}) \quad (2)$$

At 25 °C and standard conditions, these reactions impose a theoretical electrochemical stability window of 1.23 V for water, which fundamentally constrains the operating voltage of ALIBs [9, 10-12, 14]. As a result, early ALIBs suffered from limited voltage and low energy density, constraining their practical deployment.

A major breakthrough in overcoming this limitation was reported in 2015 by Suo et al. who introduced the concept of water-in-salt electrolytes [11,12]. By employing extremely high lithium salt concentrations (typically exceeding 20 mol $kg^{-1}$), the solvation structure of $Li^+$ ions is fundamentally altered, with most water molecules coordinated within the primary solvation shell. This drastically reduces the activity of free water, kinetically suppressing both hydrogen and oxygen evolution reactions and extending the practical electrochemical stability window to nearly 3 V [11, 12].

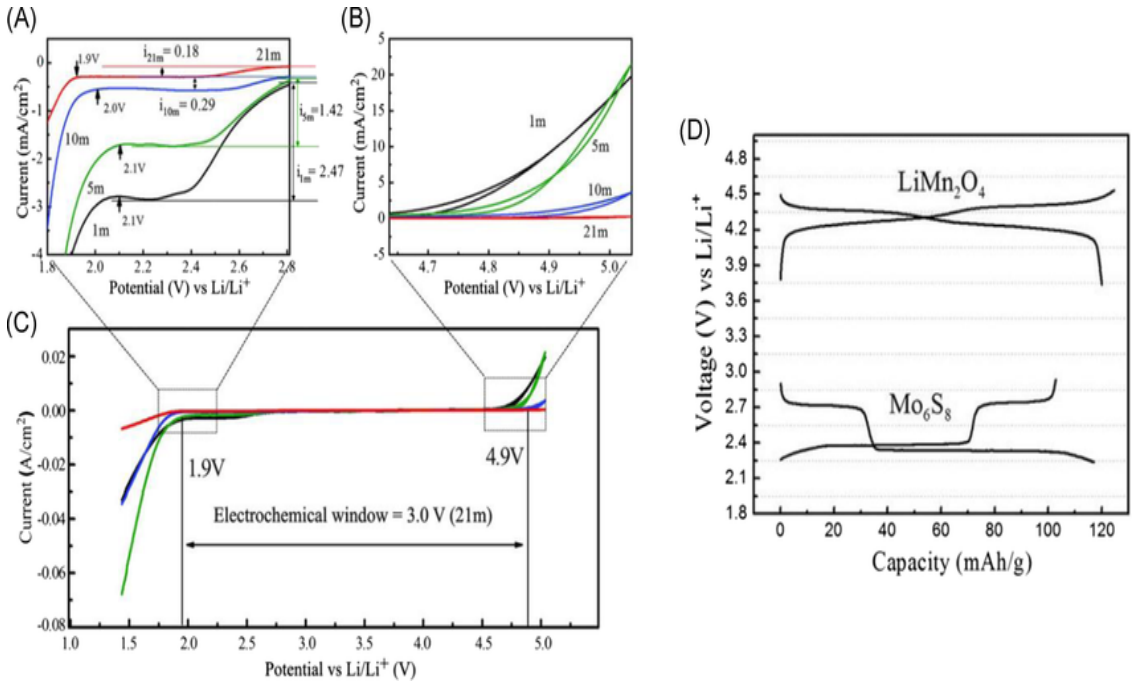



***Figure 1.2222:*** *(A) Complex LiTFSI-dependent cathodic behavior at the Al anode, (B) anodic behavior at a Ti cathode, (C) WiSE electrochemical stability window, and (D) the charge/discharge behavior of the $Mo_6S_8$ anode and $LiMn_2O_4$ cathode with WiSE. Reproduced from [12].*

As illustrated in Figure 1.2, the electrochemical stability of water can be significantly extended through the use of highly concentrated “water-in-salt” electrolytes (WiSE)

[12, 19]. Figure 1.2(A) presents cyclic-voltammetry measurements at an Al electrode, demonstrating that the cathodic behavior of the system strongly depends on the concentration of LiTFSI [12]. As the salt concentration increases, the onset of hydrogen evolution shifts toward more negative potentials, indicating suppression of water reduction and improved cathodic stability [12, 19].

Figure 1.2(B) shows the corresponding anodic behavior measured at a Ti electrode. In a similar manner, increasing electrolyte concentration progressively shifts the onset of oxygen evolution to higher potentials, thereby expanding the oxidative stability limit of the aqueous electrolyte [12]. The combined effect of these cathodic and anodic shifts is summarized in Figure 1.2(C), which illustrates the resulting electrochemical stability window of the WiSE electrolyte. In highly concentrated systems, this window can approach approximately 3.0 V, far exceeding the conventional thermodynamic stability limit of water [11, 12, 19].

This remarkable expansion is attributed to the altered solvation environment of $Li^+$ ions in highly concentrated electrolytes, where most water molecules participate in $Li^+$ coordination and the activity of free water is substantially reduced [12, 19]. As a result, both hydrogen and oxygen evolution reactions become kinetically suppressed, while interfacial passivation phenomena may further contribute to enhanced electrochemical stability [12, 19].

Finally, Figure 1.2(D) demonstrates the practical implications of this electrolyte-engineering strategy through galvanostatic charge–discharge measurements of a full aqueous cell employing a $Mo_6S_8$ anode and a $LiMn_2O_4$ cathode [12]. The stable electrochemical behavior observed confirms that highly concentrated electrolytes enable aqueous lithium-ion batteries to operate reversibly at voltages previously considered inaccessible for water-based systems [12, 20]. Overall, Figure 1.2 provides direct evidence that electrolyte engineering is a key pathway for expanding the operational voltage window of aqueous lithium-ion batteries and enabling the development of high-voltage aqueous energy-storage systems [12, 19, 20].

Representative examples of conventional lithium-ion batteries (LIBs) and aqueous lithium-ion battery (ALIB) configurations reported in the literature are summarized in Table 1.1. Commercial LIB systems such as $LiCoO_2$–graphite and Ni-rich layered oxide cells demonstrate high operating voltages and high energy density but rely on flammable organic electrolytes and therefore require complex safety management strategies [3, 8]. In contrast, aqueous lithium-ion batteries employing cathodes such as $LiMn_2O_4$ or $LiFePO_4$ paired with $Li_4Ti_5O_{12}$ anodes operate at lower voltages (typically ≈1.8–1.9 V) but exhibit significantly improved safety and remarkable cycling stability, often exceeding 3000–5000 cycles with Coulombic efficiencies approaching 100 % [11]. Recent advances in electrolyte engineering, particularly the development of water-in-salt electrolytes and gel-polymer aqueous systems, have further expanded the accessible electrochemical stability window of water and enabled higher-voltage aqueous battery configurations [11, 12]. Overall, the comparison presented in Table 1.1 highlights the fundamental trade-off between energy density and intrinsic safety, illustrating why aqueous lithium-ion batteries are increasingly considered a promising alternative for applications where long-term stability, safety, and environmental compatibility are prioritized.

| System / Electrodes | Electrolyte | Average cell voltage (V) | Specific capacity (mAh $g^{-1}$) | Cycle life (cycles) | Coulombic efficiency (%) | Features | Ref |
|---|---|---|---|---|---|---|---|
| **$LiCoO_2$ - Graphite (commercial LIB)** | 1 M $LiPF_6$ in EC/DMC (1:1) | 3.7 | ≈ 150 | > 1000 | > 99 | High energy density, flammable organic electrolyte; safety concerns | [3] |
| **NMC811 - Graphite** | 1 M $LiPF_6$ in EC/EMC | 3.8 | ≈ 180 | 2000 | > 99 | High energy density (≈ 250 Wh $kg^{-1}$); Ni-rich layered cathode | [8] |
| **$LiMn_2O_4$ - LTO (ALIB)** | 1 M $Li_2SO_4$ (aq.) | ≈ 1.8 | ≈ 110 | > 5000 | ≈ 99 | High stability, safe operation | [11] |
| **$LiFePO_4$ - LTO (ALIB)** | 2 M $LiNO_3$ (aq.) | ≈ 1.9 | ≈ 120 | > 3000 | ≈ 98 | Excellent reversibility, moderate voltage | [11] |
| **$LiMn_2O_4$ - $Mo_6S_8$ (ALIB)** | 21 m LiTFSI (WiSE) | ≈ 3.0 | ≈ 100 | > 5000 | ≈ 99 | Extended window; WiSE electrolyte | [12] |
| **$LiFePO_4$ - $Li_4Ti_5O_{12}$ (GPE)** | PVA–$Li_2SO_4$ gel | 1.8 | ≈ 115 | 3000 | ≈ 98 | Flexible polymer system | [11] |

***Table 1.1111:*** *Comparison of representative organic and aqueous LIB systems.*

Overall, although ALIBs currently lag behind conventional LIBs in terms of voltage and energy density, their combination of safety, durability, low cost, and environmental friendliness positions them as strong candidates for large-scale and stationary energy-storage applications [8, 11]. Continued advances in electrolyte engineering and electrode design are rapidly strengthening the case for aqueous systems as a key component of sustainable energy-storage technologies [8, 11].

Within this framework, the present thesis focuses on ALIB systems employing lithium titanate as a model anode material, aiming to investigate electrolyte–electrode interactions and evaluate the role of electrolyte chemistry in determining electrochemical stability and performance. By emphasizing interfacial mechanisms rather than solely material capacity, this work seeks to contribute to the development of safer and more sustainable aqueous energy-storage technologies.

## 1.2 Operating Principle of ALIBs

ALIBs operate according to the same fundamental electrochemical principle as conventional non-aqueous LIBs, namely the reversible intercalation and deintercalation

of $Li^+$ ions between two host electrodes [2]. During charging, lithium ions are extracted from the cathode lattice and inserted into the anode structure, while electrons flow through the external circuit to maintain charge neutrality. During discharge, the reverse processes occur, delivering electrical energy to the external load. The overall cell voltage is determined by the difference between the equilibrium potentials of the cathode and anode, as described by classical electrochemical thermodynamics [10], given by the equation (3) [12, 18]:

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} \quad (3)$$

In aqueous systems, water decomposes via the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER), which define the lower and upper thermodynamic limits of aqueous electrolytes, respectively [9-12]. If either electrode potential exceeds these limits during operation, parasitic gas-evolution reactions occur, leading to efficiency losses, electrolyte consumption, and progressive degradation of electrochemical performance.

Electrode potentials in aqueous electrochemical systems are commonly reported with respect to reference electrodes such as the standard hydrogen electrode (SHE), the silver/silver chloride electrode (Ag/AgCl), or the saturated calomel electrode (SCE) [10, 12 - 14]. Accurate conversion between these reference scales is essential for consistent interpretation of electrochemical data and for meaningful comparison between aqueous and non-aqueous battery systems [10]. For instance, a potential of 1.23 V versus SHE corresponds approximately to 3.03 - 3.05 V versus $Li^+/Li$, a conversion frequently used to relate aqueous electrochemistry to conventional LIB conventions [9, 10, 12]. At 25 °C, the relationships between common reference electrodes can be expressed as follows [12, 19]:

$$E(\text{Li}^+/\text{Li}) = E(\text{SHE}) - 3.04\ \text{V} \quad (4)$$
$$E(\text{Ag/AgCl}) = E(\text{SHE}) - 0.197\ \text{V} \quad (5)$$
$$E(\text{SCE}) = E(\text{SHE}) - 0.241\ \text{V} \quad (6)$$

These conversion relationships are indispensable for evaluating the electrochemical stability window of aqueous electrolytes and for ensuring consistency in the interpretation of redox potentials, cyclic voltammetry data, and full-cell voltages across different experimental configurations [10].

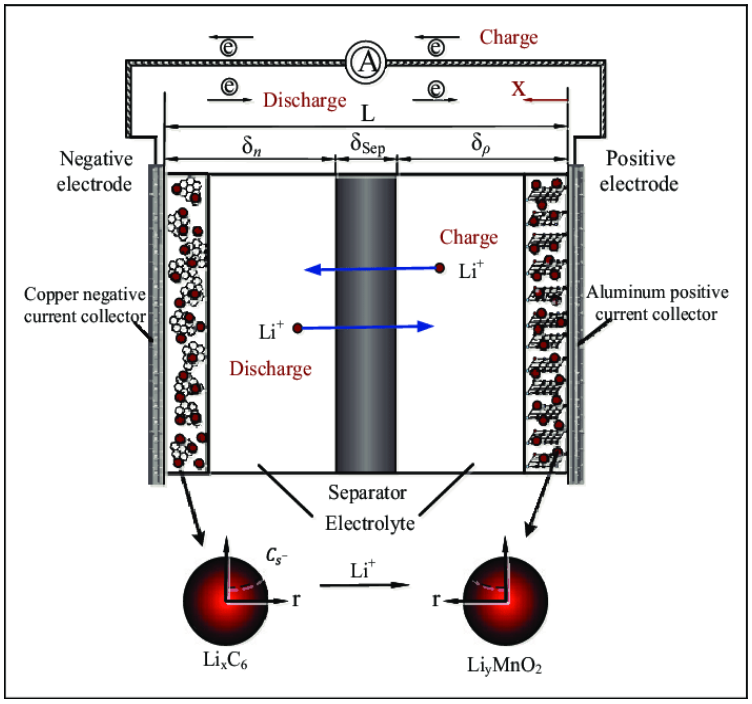



***Figure 1.3333:*** *Schematic illustration of a LIB during discharge/charge showing coupled ionic and electronic transport processes. Conceptual illustration based on LIB operating principles described in the literature [2, 10].*

As illustrated in Figure 1.3 [2, 10], which schematically represents the general operating mechanism of LIBs, lithium ions migrate through the electrolyte and separator between the two electrodes, while electrons are transported through the external circuit. This coupled ionic–electronic transport mechanism is common to both aqueous and non-aqueous LIBs and forms the fundamental basis of energy storage and release in these systems [2, 20].

In ALIBs, the same operational principle takes place under significantly different electrochemical constraints imposed by the presence of water as the solvent [9, 10]. Unlike organic systems, where the electrolyte primarily serves as an ion-transport medium within a wide electrochemical stability window, aqueous electrolytes actively participate in interfacial reactions and introduce additional thermodynamic limits associated with water decomposition [9]. Consequently, although the charge-storage mechanism illustrated in Figure 1.3 remains conceptually identical, aqueous systems must operate within a restricted potential range defined by hydrogen and oxygen evolution reactions, which strongly influence electrode selection and interfacial kinetics [9, 10].

In aqueous electrolytes, the high dielectric constant of water promotes fast ionic transport but simultaneously imposes a narrow thermodynamic stability window due to water decomposition reactions [4, 9]. To overcome this limitation, electrolyte-engineering strategies have been developed using extremely high salt concentrations to alter the coordination environment of $Li^+$ ions such that most water molecules participate in ion solvation and the activity of free water is significantly reduced [12]. This modification kinetically suppresses hydrogen and oxygen evolution reactions and extends the practical electrochemical stability window to approximately 2.8 – 3.0 V [11

- 13]. Within this expanded voltage window, several electrode materials previously considered incompatible with aqueous electrolytes, including $LiMn_2O_4$, $LiNi_{0.5}Mn_{1.5}O_4$, and $LiCoO_2$, can undergo reversible electrochemical reactions with significantly reduced parasitic decomposition [11, 12]. In parallel, complementary electrolyte strategies such as gel-polymer electrolytes and hybrid aqueous systems further enhance stability by restricting water mobility and modifying electrode–electrolyte interfacial chemistry [11]. These developments collectively demonstrate that electrolyte engineering can partially overcome the intrinsic thermodynamic limitations of water [11, 12].

Beyond bulk electrolyte properties, interfacial phenomena play a decisive role in aqueous battery operation. Modified solvation environments in highly concentrated and gel-based electrolytes promote the formation of inorganic-rich surface layers analogous to the solid–electrolyte interphase observed in non-aqueous LIBs, improving Coulombic efficiency and cycling stability [4, 12]. However, the effectiveness of such stabilization strongly depends on the intrinsic properties of the electrode material [10].

In that perspective, anode selection remains critical because the negative electrode operates close to the hydrogen evolution limit [9]. Among candidate materials, $Li_4Ti_5O_{12}$, LTO has emerged as one of the most suitable anodes for ALIBs due to its relatively high operating potential, zero-strain lithiation mechanism, and stable interfacial behavior [14]. Consequently, the present work focuses on LTO-based aqueous systems, where electrolyte engineering and interfacial stability can be systematically investigated without interference from mechanically induced degradation mechanisms. The following section therefore examines anode materials used in aqueous systems, with emphasis on the structural and electrochemical characteristics that make LTO a benchmark material for safe aqueous battery operation.

## 1.3 Anodes Used in Aqueous Systems

The selection of an appropriate anode material is a critical factor in the design of aqueous lithium-ion batteries, as it directly influences both the accessible voltage window and the electrochemical stability of the system. In conventional non-aqueous lithium-ion batteries, graphite and metallic lithium are widely employed due to their extremely low redox potentials (≈ 0 V vs $Li^+/Li$), which enable high cell voltages and energy density [3]. However, under aqueous conditions such low potentials promote rapid parasitic reactions, including hydrogen evolution and gas formation, leading to irreversible electrode degradation and poor cycling stability [9]. Consequently, significant research efforts have focused on identifying alternative anode materials that operate at slightly higher potentials while still allowing reversible lithium-ion insertion and maintaining chemical stability in aqueous electrolytes [11].

Among the various candidates explored, titanium-based oxides—most notably titanium dioxide ($TiO_2$) and lithium titanate ($Li_4Ti_5O_{12}$, LTO)—have emerged as the most reliable anode materials for aqueous operation [11]. These compounds combine moderately positive lithiation potentials, excellent chemical inertness in water, non-toxicity, and outstanding structural stability [11]. Their mechanical robustness arises

from minimal lattice distortion during $Li^+$ insertion and extraction (typically <1%), which suppresses particle cracking and preserves electronic contact within the electrode [14]. In addition, their environmental compatibility, associated with earth-abundant elements and relatively low-temperature synthesis routes, further strengthens their suitability for sustainable energy-storage technologies [8].

Titanium dioxide exists in several polymorphic forms, including anatase, rutile, and brookite, all of which can host lithium ions through the $Ti^{4+}/Ti^{3+}$ redox couple, as comprehensively reviewed by Chen and Mao [15]. In aqueous systems, the principal limitations of $TiO_2$ arise from sluggish $Li^+$ diffusion kinetics and intrinsically low electronic conductivity [15]. Although its lithiation potential (≈1.7–1.8 V vs $Li^+/Li$) nominally lies within the stability window of water, kinetic constraints severely limit its practical rate capability [15]. As a result, extensive research has focused on transport enhancement strategies rather than capacity maximization.

Nanostructuring approaches, such as nanotubes, nanorods, and mesoporous architectures, effectively shorten $Li^+$ diffusion paths, while surface engineering techniques including carbon coating and oxygen-vacancy introduction enhance electronic conductivity and interfacial charge transfer [15]. For example, Chen et al. demonstrated that oxygen-deficient $TiO_{2-x}$ nanosheets exhibit significantly improved rate performance in aqueous electrolytes owing to enhanced electronic conductivity and accelerated interfacial kinetics [16]. Similarly, numerous studies summarized by Chen and Mao have shown that carbon-modified $TiO_2$ electrodes display improved cycling stability due to stabilized surface chemistry and reduced parasitic reactions [15].

Within the aqueous context, LTO has attracted particular attention due to its near-zero volume change (~0.2%) during lithiation and delithiation, first reported by Ohzuku et al. [14], which eliminates mechanical degradation and enables exceptional cycling stability. Nevertheless, the equilibrium potential of LTO (~1.55 V vs $Li^+/Li$) corresponds to approximately −1.7 V versus common aqueous reference electrodes (Ag/AgCl or SCE at 25 °C) according to the electrode-potential framework established by Trasatti [13]. This distinction highlights an important conceptual point: although LTO is intrinsically stable in non-aqueous systems, direct operation in conventional aqueous electrolytes positions its working potential close to the cathodic stability limit of water [9], making interfacial reactions unavoidable without appropriate electrolyte or interface engineering.

Therefore, the successful implementation of LTO in ALIBs depends not solely on intrinsic material stability but on the combined optimization of electrode surface chemistry and electrolyte environment, which together regulate interfacial reactions and enable reversible operation under aqueous conditions, consistent with electrolyte–interphase principles discussed by Xu and classical electrochemical theory described by Bard and Faulkner [4, 10].

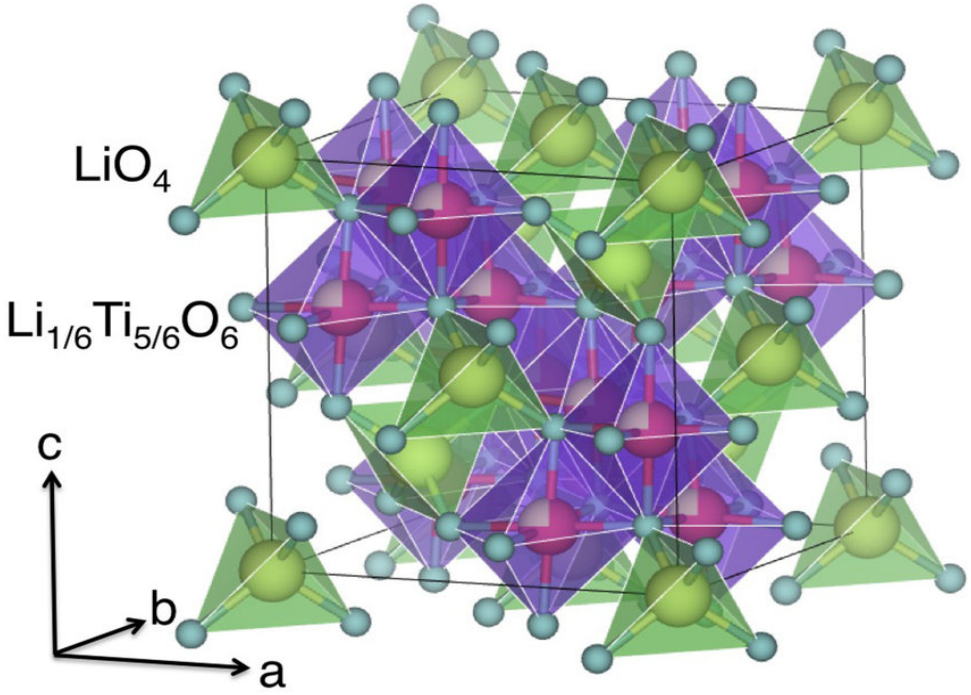



***Figure 1.4444:*** *Crystal structure of spinel $Li_4Ti_5O_{12}$. Lithium ions occupy the tetrahedral 8a sites, while the octahedral 16d sites are shared by $Ti^{4+}$ and a fraction of $Li^+$ ions ($Li_{1/6}Ti_{5/6}$). In the related spinel $LiTi_2O_4$, the 16d sites are occupied by mixed-valence $Ti^{3.5+}$. Adopted from Ohzuku et al. [14].*

As illustrated in Figure 1.4 [14], $Li_4Ti_5O_{12}$ crystallizes in a cubic spinel structure (space group *Fd-3m*) [27]. The structure consists of a three-dimensional framework of edge-sharing $TiO_6$ octahedra and $LiO_4$ tetrahedra. In this spinel lattice, lithium ions occupy the tetrahedral 8a crystallographic sites, whereas the octahedral 16d sites are predominantly occupied by $Ti^{4+}$ together with a small fraction of $Li^+$ ions, often described as $Li_{1/6}Ti_{5/6}$ [14]. The remaining octahedral 16c sites serve as the insertion sites for lithium during electrochemical lithiation. This crystallographic arrangement provides interconnected three-dimensional diffusion pathways for $Li^+$ transport and underpins the near-zero-strain lithiation mechanism of $Li_4Ti_5O_{12}$ [14].

Unlike many insertion anodes that undergo substantial lattice distortion during cycling, the spinel framework of LTO exhibits extremely small volume variation (≈0.2 %), maintaining structural integrity and preserving interparticle contact [4, 14, 22]. This exceptional structural stability is the primary reason why $Li_4Ti_5O_{12}$ is widely regarded as a benchmark anode material for long-life lithium-ion and aqueous lithium-ion battery systems.

Recent studies have demonstrated that this challenge can be effectively addressed by combining surface protection strategies with electrolyte engineering. For example, defect and surface engineering approaches in titanate-based electrodes, as reported by Chen et al., significantly improve interfacial kinetics and cycling stability through enhanced electronic conductivity and facilitated $Li^+$ transport [16]. The effectiveness of such approaches arises from the formation of modified surface structures that mitigate direct electron transfer to water molecules while preserving $Li^+$ transport pathways.

Similarly, the development of highly concentrated electrolytes introduced by Suo et al., has enabled stable operation of electrode materials previously considered incompatible with aqueous environments by suppressing hydrogen evolution and expanding the practical electrochemical stability window [12]. In these systems, stability is attributed to reduced water activity and the formation of inorganic-rich interphases that passivate electrode surfaces [4, 12].

By contrast, comprehensive analyses of ALIBs summarized by Wang et al. indicate that conventional neutral aqueous electrolytes remain susceptible to gradual interfacial degradation despite initially high Coulombic efficiency [11]. This behavior underscores that Coulombic efficiency alone is insufficient to assess long-term stability in aqueous systems and that uncontrolled water activity at the interface ultimately governs degradation pathways [9, 11]. Collectively, these studies emphasize that the principal limitation of aqueous LTO systems does not stem from the bulk material itself but rather from the interfacial chemistry between the electrode and the electrolyte [4].

Beyond LTO, several alternative titanium- and niobium-based anodes have been investigated for ALIBs, including NASICON-type $LiTi_2(PO_4)_3$, $Nb_2O_5$, and defect-engineered $TiO_2$ (B) phases [11, 15, 16]. While these materials can achieve higher specific capacities (typically 180–200 mAh $g^{-1}$) and improved $Li^+$ diffusion kinetics, they often suffer from narrower pH stability windows, partial dissolution during extended cycling, or reliance on complex synthesis routes such as templated sol–gel processing and high-temperature annealing [11, 15]. As a result, LTO remains the most balanced anode candidate—not due to its capacity, but because of its exceptional structural integrity, chemical robustness, and scalability—provided that hydrogen evolution is effectively mitigated through electrolyte and interphase design [4, 14].

To provide a clearer comparison between candidate anode materials and to highlight the rationale behind the selection of lithium titanate in ALIB research, Table 1.2 summarizes representative anode families reported in the literature, focusing on their specific capacity, structural stability, and compatibility with aqueous electrolytes [11]. Such a comparison allows rapid visualization of the fundamental trade-off between theoretical capacity and interfacial stability in water-based systems.

| **Anode Material** | **Charge Storage Mechanism** | **Theoretical Specific Capacity (mAh $g^{-1}$)** | **Structural Stability During Cycling** | **Stability in Aqueous Electrolytes** | **Main Limitation in Water** | **Ref.** |
|---|---|---|---|---|---|---|
| **Graphite** | $Li^+$ intercalation | 372 | Moderate (volume change ~10%) | Poor | Strong HER competition; unstable potential | [3, 4] |
| **$TiO_2$ (anatase)** | Intercalation | ~335 | Moderate | Limited–Moderate | Slow diffusion; surface reconstruction | [15] |

| Anode Material | Charge Storage Mechanism | Theoretical Specific Capacity (mAh $g^{-1}$) | Structural Stability During Cycling | Stability in Aqueous Electrolytes | Main Limitation in Water | Ref. |
|---|---|---|---|---|---|---|
| **$TiO_2$(B)** | Intercalation | ~300 | Improved vs anatase | Moderate | Defect-induced HER activation | [15, 16] |
| **$LiTi_2(PO_4)_3$ (NASICON)** | Intercalation | ~170 | Good | Moderate | pH sensitivity; dissolution risk | [11] |
| **$Nb_2O_5$** | Pseudocapacitive / intercalation | ~200 | Moderate | Limited | Complex synthesis; stability issues | [11] |
| **Conversion-type oxides ($Fe_3O_4$, $Mn_3O_4$)** | Conversion reactions | 600–900 | Poor | Poor | Large volume change; rapid degradation | [3, 8] |
| **$Li_4Ti_5O_{12}$ (LTO)** | Intercalation ($Ti^{4+}/Ti^{3+}$) | 175 | Excellent (≈0.2% volume change) | High | Low electronic conductivity | [4, 14] |

***Table 1.2222:*** *Comparative overview of representative anode materials investigated for ALIBs, highlighting the trade-off between theoretical capacity and electrochemical stability in water.*

As shown in Table 1.2, anodes exhibiting the highest theoretical capacities generally suffer from poor structural and interfacial stability in aqueous environments [9, 11]. Materials operating at very low electrochemical potentials, such as graphite or conversion-type oxides, strongly promote parasitic reactions including hydrogen evolution and electrolyte decomposition, which accelerate electrode degradation [4, 9]. Conversely, insertion-type oxides operating at moderately positive potentials demonstrate significantly improved compatibility with water-based electrolytes and better long-term structural stability [11].

Evidence of such degradation processes is commonly obtained through post-cycling characterization techniques. For example, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) often reveal morphological changes such as particle cracking, surface roughening, or loss of structural integrity after repeated cycling. In addition, electrochemical impedance spectroscopy (EIS) and X-ray diffraction (XRD) measurements frequently indicate increased interfacial resistance or structural distortion associated with degradation processes [4, 9, 11].

Among the various candidates, $Li_4Ti_5O_{12}$ emerges as a uniquely balanced material. Although its theoretical capacity is lower than that of several alternative anodes, its near-zero-strain lithiation mechanism, structural robustness, and comparatively stable interfacial behavior enable superior long-term cycling stability under aqueous conditions [4, 14]. This balance between stability and electrochemical reversibility explains why LTO has become a model anode material for investigating electrolyte–electrode interactions in ALIB systems [11, 14].

## 1.4 Electrolytes for Aqueous Systems

The electrolyte acts as the ionic medium that enables lithium-ion transport between the electrodes and plays a central role in the overall operation of aqueous lithium-ion batteries (ALIBs). In addition to facilitating $Li^+$ conduction, electrolyte composition strongly influences interfacial electrochemical reactions occurring at both electrodes, including hydrogen and oxygen evolution, corrosion of current collectors, and surface degradation of active materials [4]. Consequently, careful electrolyte design and optimization have become critical strategies for improving the stability, safety, and electrochemical performance of aqueous battery systems [11].

Conventional aqueous electrolytes consist of lithium salts dissolved in deionized water, including $Li_2SO_4$, $LiNO_3$, LiCl, LiOH, and LiTFSI [11]. Each salt distinctly affects ionic conductivity, viscosity, pH, corrosion behavior, and electrochemical stability [4], [11]. Among these, neutral salts such as $Li_2SO_4$ and $LiNO_3$ are most widely employed due to their chemical stability and relatively low corrosivity. Li et al. demonstrated that 1 M $Li_2SO_4$ exhibits ionic conductivities in the range of 0.05–0.08 S $cm^{-1}$ while maintaining minimal corrosion toward stainless steel and Ti-based current collectors, making it particularly suitable for LTO-based aqueous systems [17]. Similarly, Demir-Cakan et al. reported that $LiNO_3$-based electrolytes offer slightly higher ionic conductivity (≈0.10 S $cm^{-1}$) and near-neutral pH; however, extended cycling at negative potentials may induce partial nitrate reduction, leading to the formation of $NO_2^-$ or $NH_4^+$ species and gradual electrolyte modification [18].

By contrast, chloride-based electrolytes such as LiCl, although highly conductive (~$10^{-2}$ S $cm^{-1}$), are generally unsuitable for ALIBs due to severe corrosion issues. Chloride ions promote anodic dissolution of aluminum current collectors through complex formation and destabilization of the native oxide passivation layer, even at moderate potentials, as discussed in electrochemical corrosion analyses of aqueous systems [4, 11, 18]. Consequently, LiCl electrolytes are typically avoided in systems employing Ti-based anodes, where interfacial stability is critical [11].

Strongly alkaline electrolytes, such as LiOH solutions, present an additional challenge. While high alkalinity can facilitate fast ion transport, it simultaneously accelerates corrosion and parasitic reactions. Under highly basic conditions, titanium-based electrode surfaces may undergo hydroxylation and chemical modification, leading to impedance growth and capacity degradation during cycling [4, 9, 18]. Moreover, highly basic environments intensify hydrogen and oxygen evolution kinetics, thereby reducing Coulombic efficiency and compromising long-term stability [9, 10].

A major breakthrough in aqueous electrolyte design was achieved with the introduction of WiSE as mentioned previously, based on extremely high salt concentrations that dramatically reduce free-water activity. Using a 21 m LiTFSI electrolyte, Suo et al. demonstrated an expanded electrochemical stability window approaching 3.0 V, enabling the stable operation of high-voltage cathodes such as $LiMn_2O_4$ and $LiCoO_2$ in aqueous environments [12]. In these systems, the $Li^+$ solvation structure is dominated

by anions rather than water molecules, suppressing hydrogen and oxygen evolution [12, 19]. Nevertheless, subsequent studies by Yamada et al. revealed that partial hydrolysis of the $TFSI^-$ anion may generate HF and sulfonate species, potentially leading to corrosion and pH drift if not carefully controlled [19]. Thus, while LiTFSI-based WiSE electrolytes represent a technologically advanced solution, they demand precise chemical control and compatible cell components to ensure durability [12, 19].

To summarize the fundamental physicochemical characteristics of commonly used aqueous electrolytes, Table 1.3 compares their typical ionic conductivities, pH values, electrochemical stability windows, and qualitative stability behavior [11, 19].

| Electrolyte | Ionic conductivity ($S \cdot cm^{-1}$) | pH | Electrochemical window (V) | Stability / Remarks | Ref. |
|---|---|---|---|---|---|
| **$Li_2SO_4$ (1 M)** | 0.05–0.08 | ≈6.0 | 1.23 | Neutral and stable, low corrosivity, narrow voltage window | [11, 17] |
| **$LiNO_3$ (1 M)** | 0.06–0.10 | ≈6.5 | 1.4 | High conductivity, mild $NO_3^-$ reduction at low potentials | [11, 18] |
| **LiCl (1 M)** | 0.08–0.12 | ≈7.0 | 1.3 | High conductivity, $Cl^-$ oxidation and pitting corrosion | [4, 11] |
| **LiTFSI (21 m, WiSE)** | 0.01–0.03 | ≈4.5 | up to 3.0 | Wide voltage window, viscous; potential HF formation | [12, 19] |
| **LiOH (1 M)** | 0.02–0.04 | ≈13.5 | ≈1.0 | Strongly basic, promotes corrosion and $O_2$ evolution | [4, 9] |
| **$Li_2CO_3$ (sat.)** | <0.01 | ≈10 | 1.2 | Poor solubility, stable only near neutral pH | [9, 10] |
| **LiAc (1 M)** | 0.05–0.09 | ≈7.0 | 1.4 | Moderate conductivity, acetate oxidation possible | [10, 11] |
| **$Na_2SO_4$ (1 M)** | 0.07–0.10 | ≈6.5 | 1.23 | Neutral model electrolyte, compatible with Ti-based anodes | [4, 11] |

***Table 1.3333:*** Comparison of the physicochemical and electrochemical properties of typical aqueous electrolytes used in ALIBs.

The values reported in Table 1.3 represent characteristic ranges compiled from electrochemical thermodynamics and ALIB literature [4, 9 -12, 17 - 19]. Although the theoretical electrochemical stability window of water is limited to 1.23 V under standard conditions [9], kinetic overpotentials and electrolyte composition can moderately extend the practical operating voltage. In particular, electrolyte chemistry strongly influences ionic conductivity, corrosion behavior, pH stability, and interfacial reactions at both electrodes [4, 11].

The principal limitation of dilute aqueous electrolytes remains the narrow thermodynamic stability window of water (1.23 V), which restricts achievable cell voltage and electrode selection [9, 10]. To overcome this constraint, three major electrolyte-engineering strategies have emerged: water-in-salt electrolytes (WiSE) [12, 19], gel-polymer-based aqueous electrolytes [11], and localized high-concentration electrolyte concepts [19].

To clearly illustrate the fundamental limitation of dilute aqueous electrolytes and the effect of salt concentration on the electrochemical stability window, Figure 1.5 presents linear sweep voltammetry (LSV) curves recorded in aqueous electrolytes of different compositions [20]. The comparison includes a conventional dilute electrolyte (1 m $LiNO_3$), a moderately concentrated electrolyte (1 m LiTFSI), and a highly concentrated water-in-salt electrolyte (21 m LiTFSI).

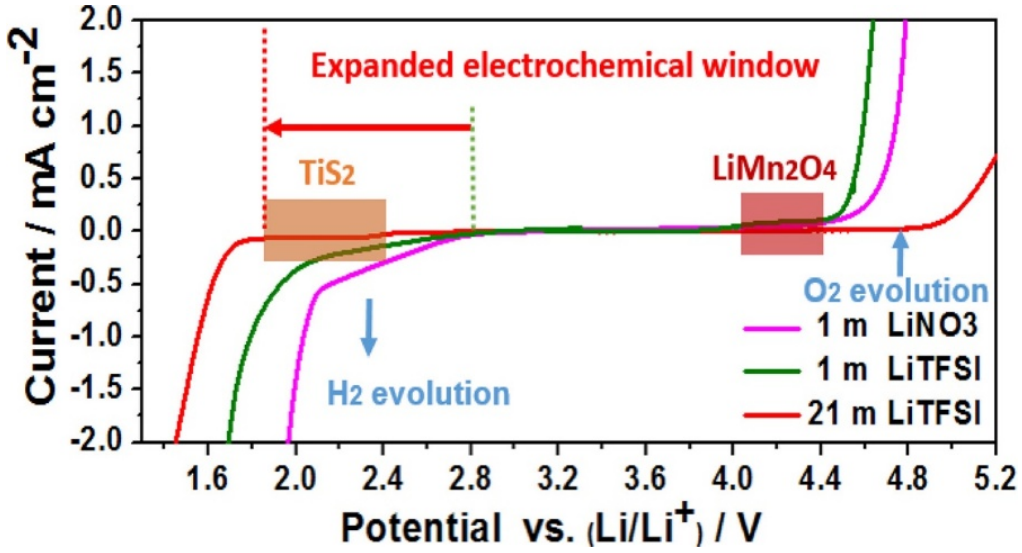



**Figure 1.5:** Electrochemical stability window of aqueous electrolytes with increasing salt concentration and corresponding operating potential ranges of selected electrode materials. Linear sweep voltammetry (LSV) curves recorded on an inert stainless-steel current collector in 1 m $LiNO_3$, 1 m LiTFSI, and 21 m LiTFSI aqueous electrolytes at a scan rate of 10 mV $s^{-1}$. The redox potential windows of $TiS_2$ and $LiMn_2O_4$ are indicated. Reproduced from Wang et al. [11].

As shown in Figure 1.5, increasing salt concentration significantly expands the electrochemical stability window of aqueous electrolytes. In highly concentrated water-in-salt systems, both the onset of hydrogen evolution and oxygen evolution are shifted to more extreme potentials, allowing electrode materials such as $TiS_2$ and $LiMn_2O_4$ to operate within the extended stability range of the electrolyte [11].

This behavior is attributed to the altered solvation structure of $Li^+$ ions in highly concentrated electrolytes, where the majority of water molecules participate in ion coordination, drastically reducing free-water activity and slowing interfacial water reduction and oxygen evolution kinetics [12, 19]. As a result, electrode materials such as $TiS_2$ and $LiMn_2O_4$, previously considered incompatible with aqueous environments, can operate reversibly within this widened voltage window, as experimentally demonstrated by Sun et al. in $LiMn_2O_4/TiS_2$ full cells using 21 m LiTFSI electrolytes [20].

Gel-polymer electrolytes (GPEs) offer a complementary stabilization strategy by confining aqueous salts within polymer matrices, thereby limiting solvent mobility and mitigating parasitic interfacial reactions. Langevin et al. demonstrated that UV-cured gel polymer electrolytes enable improved interfacial stability and safer operation in advanced aqueous lithium-ion configurations [21].

Localized high-concentration electrolyte (LHCE) concepts extend the concentrated-electrolyte strategy by preserving strong local salt coordination while improving transport properties relative to uniformly super concentrated systems. Shen et al. recently reported interfacially localized high-concentration aqueous electrolytes exhibiting electrochemical stability windows exceeding 3.0 V, ionic conductivities above 30 mS $cm^{-1}$, and stable cycling performance in rechargeable ALIBs [22]. These results confirm that electrolyte composition governs interfacial chemistry rather than bulk transport alone.

Another critical parameter in aqueous electrolyte design is pH control. During cycling, local pH fluctuations arise from proton-consuming and proton-generating side reactions, particularly hydrogen and oxygen evolution reactions, as described by classical aqueous electrochemical thermodynamics [9, 10]. As emphasized in comprehensive analyses of aqueous rechargeable systems by Demir-Cakan et al. [18], uncontrolled pH shifts can accelerate current collector corrosion, induce dissolution of transition-metal oxides, and destabilize electrode interfaces. Furthermore, concentrated-electrolyte studies by Yamada et al. [19] highlight that interfacial stability is strongly coupled to local proton activity and solvation structure. Near-neutral electrolytes generally provide improved stability for titanium-based anodes, whereas acidic environments favor transition-metal dissolution, and alkaline conditions accelerate hydrogen evolution kinetics [18, 19]. Buffering strategies and careful salt selection are therefore commonly employed to mitigate pH drift and suppress voltage instability during prolonged cycling [18].

Finally, electrolyte selection must be compatible with current collectors and binder systems. As discussed by Pourbaix in classical corrosion theory [9], metal stability in aqueous media is intrinsically pH- and potential-dependent. Comparative electrolyte studies by Li et al. [17] further demonstrate that anion chemistry significantly influences corrosion behavior and electrochemical stability. Titanium, stainless steel, and carbon-based substrates exhibit superior corrosion resistance in neutral aqueous electrolytes, whereas copper and aluminum are susceptible to dissolution in chloride- or nitrate-containing media under polarized conditions [17, 18]. Hydrophilic binder systems such as carboxymethyl cellulose (CMC) and styrene–butadiene rubber (SBR) are widely adopted in aqueous processing routes due to their chemical compatibility and enhanced electrolyte wettability, as broadly discussed in electrolyte and interphase reviews by Xu and co-workers [4].

In summary, advances in electrolyte engineering have significantly expanded the voltage window, safety, and interfacial stability of ALIBs. The pioneering work of Suo

et al. on water-in-salt electrolytes [12], the mechanistic analyses of concentrated systems by Yamada et al. [19], and the full-cell demonstrations by Sun et al. [20] collectively illustrate how electrolyte composition governs both bulk transport and interfacial chemistry. Nevertheless, the intricate coupling between electrolyte composition and anode interfacial reactions remains a key challenge. The following section therefore focuses on the remaining limitations of anodes coupled with aqueous electrolytes, emphasizing hydrogen evolution, surface instability, and degradation mechanisms that govern long-term reversibility.

While the preceding sections analyzed the physicochemical characteristics of individual aqueous electrolytes and electrolyte-engineering strategies, a full-cell perspective is required to assess their practical electrochemical impact. In operational battery systems, metrics such as average voltage, specific capacity, Coulombic efficiency, and cycle life emerge from the coupled interaction between electrode materials and electrolyte chemistry rather than from electrolyte properties alone [11, 18].

To provide a comparative framework, Table 1.4 compiles representative literature data for conventional non-aqueous lithium-ion batteries together with aqueous and hybrid electrolyte configurations, including dilute aqueous electrolytes, water-in-salt systems, gel-polymer electrolytes, and localized high-concentration strategies [12, 19, 20]. This comparison enables a quantitative evaluation of how electrolyte design governs voltage-window expansion, interfacial stability, and long-term electrochemical performance across different lithium-ion battery architectures.

| Electrolyte strategy | Representative system | Electrochemical window (V) | Ionic conductivity ($S \cdot cm^{-1}$) | Interfacial stability | Key Advantages | Main limitations | Ref. |
|---|---|---|---|---|---|---|---|
| **Dilute aqueous** | 1–2 M $Li_2SO_4$, $LiNO_3$ | 1.2–1.4 | $10^{-2}$–$10^{-1}$ | Moderate | Low cost, high safety | HER, Low voltage | [11, 18] |
| **WiSE** | 21 m LiTFSI | up to ~3.0 | ~$10^{-2}$ | High | Suppressed HER/OER, high voltage | High viscosity, cost | [12, 19, 20] |
| **GPE** | PVA–$Li_2SO_4$, PAM gels | ~1.8–2.0 | $10^{-3}$–$10^{-2}$ | High | No leakage, mechanical safety | Lower conductivity | [18] |
| **LHCE** | LiTFSI + sulfolane | ~3.0 | >WiSE | Very high | Lower viscosity, stable SEI/ESI | Complex chemistry | [19] |

***Table 1.4444:*** *Comparison of electrolyte engineering strategies in LIBs.*

As summarized in Table 1.4, conventional lithium-ion batteries based on carbonate electrolytes operate at high average voltages of approximately 3.7–3.8 V and deliver superior gravimetric energy densities, as extensively discussed by Xu, Armand, and Tarascon [4, 8]. However, these advantages are accompanied by intrinsic safety

concerns associated with flammable organic solvents and the need for complex safety management strategies [4].

In contrast, aqueous lithium-ion batteries employing neutral or mildly concentrated electrolytes (e.g., $Li_2SO_4$ or $LiNO_3$) typically operate at lower voltages in the range of 1.8–1.9 V, yet demonstrate remarkable cycling stability and high Coulombic efficiency, as reviewed by Wang et al. and Demir-Cakan et al. [11, 18]. In addition, recent developments in hybrid electrolyte systems—such as water-in-salt and gel-polymer formulations—have partially mitigated this voltage limitation while preserving the inherent safety and environmental advantages of aqueous systems [12, 19].These characteristics highlight the suitability of aqueous and hybrid lithium-ion battery systems for stationary and grid-level applications, where safety, durability, and operational reliability often outweigh the need for maximum energy density.

Importantly, pioneering work by Suo et al. on water-in-salt electrolytes [12], further analyzed mechanistically by Yamada et al. [19] and experimentally validated in full cells by Sun et al. [20], demonstrated that highly concentrated electrolytes can expand the practical electrochemical stability window of water to nearly 3.0 V. Such electrolyte-engineering strategies significantly narrow the performance gap between aqueous and non-aqueous systems while maintaining intrinsic non-flammability and improved safety.

Overall, Table 1.4 supports the conclusion that ALIBs constitute a competitive alternative for applications prioritizing safety, durability, and sustainability, particularly when electrolyte design is carefully optimized to regulate interfacial chemistry and suppress parasitic reactions [18, 19].

## 1.5 Limitations of Anodes in Aqueous Systems

Despite the significant safety, environmental, and economic advantages of ALIBs, their widespread implementation remains constrained by fundamental limitations associated with the anode–electrolyte interface [18]. In contrast to organic electrolytes, water-based systems operate within a chemically reactive environment in which parasitic reactions compete directly with lithium-ion intercalation processes, as dictated by aqueous electrochemical thermodynamics [9], [10]. These interfacial phenomena progressively affect both electrode surfaces and electrolyte composition, ultimately influencing Coulombic efficiency, rate capability, and long-term cycling stability [18, 19].

Rather than representing intrinsic bulk material failure, these limitations primarily arise from the thermodynamic instability of water at negative potentials and the resulting competition between lithium insertion and hydrogen evolution reactions [9, 19]. Even in expanded electrochemical windows achieved through water-in-salt electrolytes, interfacial reactions remain kinetically relevant at highly reducing potentials [12, 19]. Consequently, the performance of anodes coupled with aqueous electrolytes is

governed largely by interfacial chemistry and electrolyte compatibility rather than by structural degradation of the active material itself [18].

Understanding these limitations has guided the development of targeted stabilization strategies aimed at improving aqueous battery performance. Current research therefore focuses on approaches that regulate electrode–electrolyte interactions, including surface engineering, electrolyte optimization, lattice modification, and electrode architecture design [12, 18, 19]. The following subsections analyze the dominant interfacial limitations affecting anodes and discuss representative strategies proposed in the literature to mitigate their impact and enable stable long-term operation in aqueous electrolytes.

### 1.5.1 Interfacial Instability and Hydrogen Evolution

As established by classical aqueous electrochemical thermodynamics [9, 10], even modest local overpotentials near the reduction limit of water can initiate hydrogen evolution. This leads to electrolyte consumption, gas generation, and dynamic local pH fluctuations. The repeated nucleation and detachment of hydrogen bubbles disrupt the electrode–electrolyte contact, generate localized current-density inhomogeneities, and induce mechanical stresses within the porous electrode structure [18, 19].

In conventional non-aqueous lithium-ion batteries, interfacial stability is ensured by the formation of a solid electrolyte interphase (SEI), which electronically passivates the anode while remaining permeable to $Li^+$ ions, as extensively reviewed by Xu [4]. In aqueous environments, however, maintaining an analogous stable SEI is inherently challenging. Most inorganic species formed via electrolyte decomposition, including LiOH and $Li_2CO_3$, exhibit significant solubility or mechanical fragility in water, while the continuous presence of water promotes ongoing surface reactions [12, 18, 19].

These degradation mechanisms are schematically summarized in Figure 1.6, which illustrates several coupled electrochemical and mechanical failure processes occurring in lithium-ion cells. At the anode side, parasitic reactions between the electrolyte and the electrode surface lead to continuous formation and decomposition of surface films, gas evolution, and lithium plating under unfavorable operating conditions. These processes can induce particle cracking, loss of electrical contact, and progressive growth of interfacial resistance.

In addition, electrolyte decomposition products may trigger binder degradation and destabilization of the electrode architecture, while transition-metal dissolution from the cathode can further accelerate interfacial degradation. Corrosion of the current collector and structural disordering of active materials may also occur during prolonged cycling. Although these mechanisms have been widely documented for conventional lithium-ion batteries, they can become even more pronounced in aqueous systems due to the presence of water and the absence of a stable, self-passivating solid–electrolyte interphase (SEI) layer [4, 18]. As a result, understanding and mitigating such

degradation pathways remains a key challenge for the development of durable aqueous lithium-ion batteries.

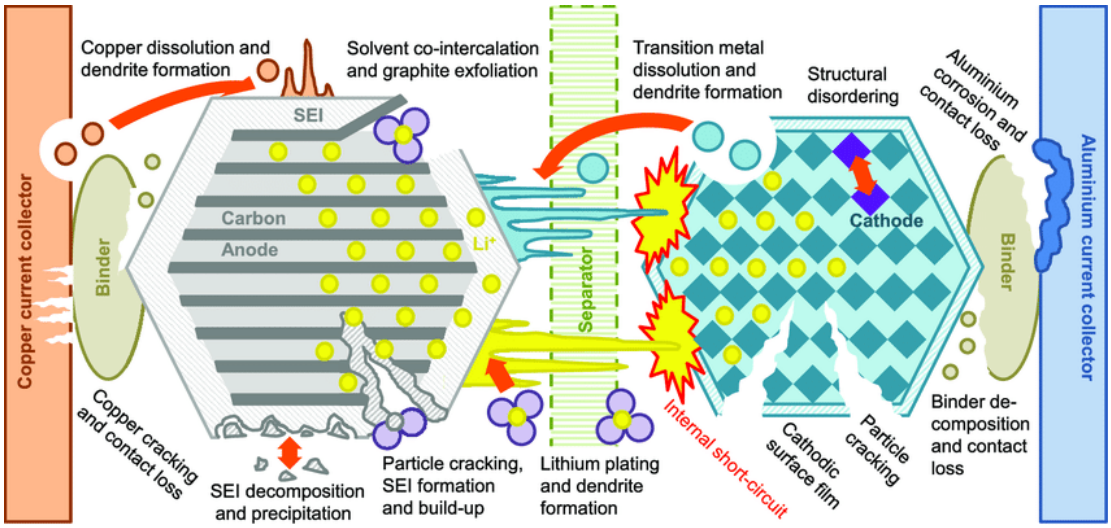



**Figure 1.6:** Schematic illustration of major degradation mechanisms in lithium-ion cells, including electrolyte decomposition, gas evolution, surface film instability, particle cracking, binder degradation, transition-metal dissolution, and current collector corrosion occurring at electrode–electrolyte interfaces during prolonged cycling. Adapted from R. Demir-Cakan et al. [18].

### 1.5.2 Chemical Dissolution and Surface Degradation

Beyond gas evolution, chemical instability of the anode surface represents an additional degradation pathway in aqueous systems. As discussed in aqueous battery reviews by Demir-Cakan et al. [18], transition-metal oxides can undergo electrolyte-dependent surface reactions influenced strongly by local pH conditions. Titanium-based anodes such as $TiO_2$ and $Li_4Ti_5O_{12}$ (LTO), although structurally robust in non-aqueous environments [14], may experience gradual surface reconstruction under aqueous operation. Under mildly acidic conditions, partial $Ti^{4+}$ dissolution may occur, whereas alkaline environments promote hydroxide attack on Ti–O bonds, potentially forming amorphous titanium oxyhydroxide layers that impede lithium-ion diffusion [15, 18]. Local pH shifts induced by HER further accelerate these processes, increasing interfacial resistance and limiting rate performance [9, 19].

### 1.5.3 Surface Engineering Strategies

To suppress parasitic reactions and stabilize the anode–electrolyte interface, extensive research has focused on surface engineering approaches designed to decouple lithium insertion from direct water contact. As emphasized in aqueous battery reviews by Demir-Cakan et al. [18] and in concentrated-electrolyte analyses by Yamada et al. [19], interfacial stabilization is a prerequisite for enabling long-term operation in water-based systems.

Among the most effective strategies, ultrathin oxide coatings deposited via atomic layer deposition (ALD) provide conformal and precisely controlled protective layers. Yoon et al. [23] demonstrated that nanometer-scale $Al_2O_3$ coatings on $Li_4Ti_5O_{12}$ (LTO)

significantly enhance cycling stability by suppressing surface degradation and limiting direct electrolyte interaction [21]. The ultrathin $Al_2O_3$ layer acts as an electronically insulating yet ionically permeable barrier, mitigating interfacial side reactions while preserving $Li^+$ transport pathways.

In parallel, sol–gel–derived oxide coatings offer a scalable alternative to ALD processing. As discussed in materials chemistry analyses by Chen and Mao [15], oxide surface modifications can regulate Ti–O surface chemistry and reduce susceptibility to hydroxide attack in aqueous environments. Such coatings function by forming compact interfacial layers that limit proton access and stabilize surface coordination environments.

Phosphate-based surface modifications represent an additional stabilization route. Phosphate-containing interphases are known to buffer local acidity and reduce transition-metal dissolution, while maintaining $Li^+$ conductivity through ionically conductive surface phases [18, 19]. These strategies are particularly relevant for titanium-based anodes, where surface dissolution rather than bulk structural collapse governs degradation.

Carbonaceous coatings provide a complementary approach by enhancing electronic conductivity and modifying surface wettability. As demonstrated in defect-engineered $Li_4Ti_5O_{12}$–$TiO_2$ nanosheets by Chen et al. [16], surface structural modification improves charge-transfer kinetics and rate capability. In aqueous systems, carbon layers can additionally reduce hydrogen adsorption kinetics and limit bubble nucleation sites, thereby mitigating HER-induced degradation.

Collectively, these surface engineering strategies confirm that the long-term stability of anodes depends predominantly on interfacial regulation rather than intrinsic bulk material robustness. Even structurally stable materials such as LTO [14] require engineered surface protection to achieve durable performance under aqueous electrochemical conditions.

### 1.5.4 Bulk Doping and Lattice Engineering

In addition to surface modification, bulk doping and lattice engineering provide intrinsic pathways to enhance anode stability and electrochemical performance. Although LTO exhibits exceptional structural stability due to its zero-strain lithiation mechanism [14], its intrinsically low electronic conductivity remains a limiting factor. Various studies on titanium-based oxides have shown that aliovalent substitution can modify electronic structure and transport pathways, thereby improving charge-transfer kinetics and structural robustness [15, 16].

Partial substitution of $Ti^{4+}$ with higher-valent cations (e.g. …) has been reported to increase electronic conductivity and, in some cases, slightly shift the lithiation potential toward more positive values. Such shifts can reduce the thermodynamic driving force for hydrogen evolution in aqueous systems, thereby indirectly improving interfacial stability [18, 19].

## 1.6 Summary

In summary, the performance limitations of anodes coupled with aqueous electrolytes are governed primarily by interfacial chemistry rather than intrinsic bulk instability of the active materials. Hydrogen evolution, chemical dissolution, and mechanical degradation collectively restrict long-term reversibility and energy efficiency. Nevertheless, advances in surface engineering, lattice modification, electrolyte formulation, and electrode architecture have substantially mitigated these challenges. In particular, LTO-based systems have demonstrated excellent cycling stability and high Coulombic efficiency under optimized aqueous electrolyte conditions, highlighting their strong potential for safe and sustainable large-scale energy storage applications [12, 19, 20]. These developments provide the foundation for Chapter 2, which focuses on the crystallographic structure, electrochemical behavior, and surface modification strategies of $Li_4Ti_5O_{12}$ as a model anode material for advanced ALIBs.

## 1.7 References


[1] International Energy Agency, Ed., “Net Zero by 2050: A Roadmap for the Global Energy Sector,” International Energy Agency, Paris, Report, 2021. [Online]. Available: https://www.iea.org/reports/net-zero-by-2050

[2] B. Dunn, H. Kamath, and J.-M. Tarascon, “Electrical Energy Storage for the Grid: A Battery of Choices,” Science, vol. 334, no. 6058, pp. 928–935, Nov. 2011, doi: 10.1126/science.1212741.

[3] M. Armand and J.-M. Tarascon, “Building better batteries,” Nature, vol. 451, no. 7179, pp. 652–657, Feb. 2008, doi: 10.1038/451652a.

[4] K. Xu, “Electrolytes and Interphases in Li-Ion Batteries and Beyond,” Chem. Rev., vol. 114, no. 23, pp. 11503–11618, Dec. 2014, doi: 10.1021/cr500003w.

[5] X. Feng, M. Ouyang, X. Liu, L. Lu, Y. Xia, and X. He, “Thermal runaway mechanism of lithium ion battery for electric vehicles: A review,” Energy Storage Mater., vol. 10, pp. 246–267, Jan. 2018, doi: 10.1016/j.ensm.2017.05.013.

[6] L. Gaines, “The future of automotive lithium-ion battery recycling: Charting a sustainable course,” Sustain. Mater. Technol., vol. 1–2, pp. 2–7, Dec. 2014, doi: 10.1016/j.susmat.2014.10.001.

[7] G. Harper et al., “Recycling lithium-ion batteries from electric vehicles,” Nature, vol. 575, no. 7781, pp. 75–86, Nov. 2019, doi: 10.1038/s41586-019-1682-5.

[8] J.-M. Tarascon, “Key challenges in future Li-battery research,” Philos. Trans. R. Soc. Math. Phys. Eng. Sci., vol. 368, no. 1923, pp. 3227–3241, Jul. 2010, doi: 10.1098/rsta.2010.0112.

[9] M. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions. NACE International, 1974.

[10] A. J. Bard and L. R. Faulkner, Electrochemical Methods: Fundamentals and Applications, 2nd ed. Wiley, 2001.

[11] Y. Wang, J. Yi, and Y. Xia, “Recent Progress in Aqueous Lithium-Ion Batteries,” Adv. Energy Mater., vol. 2, no. 7, pp. 830–840, Jul. 2012, doi: 10.1002/aenm.201200065.

[12] L. Suo et al., “‘Water-in-salt’ electrolyte enables high-voltage aqueous lithium-ion chemistries,” Science, vol. 350, no. 6263, pp. 938–943, Nov. 2015, doi: 10.1126/science.aab1595.

[13] S. Trasatti, “The absolute electrode potential: an explanatory note (Recommendations 1986),” Pure Appl. Chem., vol. 58, no. 7, pp. 955–966, Jan. 1986, doi: 10.1351/pac198658070955.

[14] T. Ohzuku, A. Ueda, and N. Yamamoto, “Zero-Strain Insertion Material of Li [ Li1 / 3Ti5 / 3 ] O 4 for Rechargeable Lithium Cells,” J. Electrochem. Soc., vol. 142, no. 5, pp. 1431–1435, May 1995, doi: 10.1149/1.2048592.

[15] X. Chen and S. S. Mao, “Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications,” Chem. Rev., vol. 107, no. 7, pp. 2891–2959, Jul. 2007, doi: 10.1021/cr0500535.

[16] J. Chen et al., “Fabrication of Li4Ti5O12-TiO2 Nanosheets with Structural Defects as High-Rate and Long-Life Anodes for Lithium-Ion Batteries,” Sci. Rep., vol. 7, no. 1, p. 2960, Jun. 2017, doi: 10.1038/s41598-017-03149-2.

[17] J. Li, J. Jiang, B. Liu, G. Liu, D. Qian, and C. Yang, “A systematically comparative study on LiNO3 and Li2SO4 aqueous electrolytes for electrochemical double-layer capacitors,” Electrochimica Acta, vol. 274, pp. 121–130, Jun. 2018, doi: 10.1016/j.electacta.2018.04.097.

[18] R. Demir-Cakan, M. R. Palacin, and L. Croguennec, “Rechargeable aqueous electrolyte batteries: from univalent to multivalent cation chemistry,” J. Mater. Chem. A, vol. 7, no. 36, pp. 20519–20539, 2019, doi: 10.1039/C9TA04735B.
[19] Y. Yamada, J. Wang, S. Ko, E. Watanabe, and A. Yamada, “Advances and issues in developing salt-concentrated battery electrolytes,” Nat. Energy, vol. 4, no. 4, pp. 269–280, Mar. 2019, doi: 10.1038/s41560-019-0336-z.
[20] W. Sun et al., “‘Water-in-Salt’ electrolyte enabled LiMn2O4/TiS2 Lithium-ion batteries,” Electrochem. Commun., vol. 82, pp. 71–74, Sep. 2017, doi: 10.1016/j.elecom.2017.07.016.
[21] S. A. Langevin et al., “UV-cured gel polymer electrolytes with improved stability for advanced aqueous Li-ion batteries,” Chem. Commun., vol. 55, no. 87, pp. 13085–13088, 2019, doi: 10.1039/C9CC06207F.
[22] G. Shen et al., “Interfacially-localized high-concentration electrolytes for high-performance rechargeable aqueous lithium-ion batteries,” EES Batter., vol. 1, no. 2, pp. 273–286, 2025, doi: 10.1039/D4EB00036F.
[23] J. K. Yoon et al., “Highly-Stable Li4Ti5O12 Anodes Obtained by Atomic-Layer-Deposited Al2O3,” Materials, vol. 11, no. 5, p. 803, May 2018, doi: 10.3390/ma11050803.

# 2. Structural and Electrochemical Characteristics of LTO Anodes

## 2.1 Structure and Characteristics of Lithium Titanate

Lithium titanate ($Li_4Ti_5O_{12}$, LTO) is a well-established spinel-structured anode material widely recognized for its outstanding structural stability during electrochemical cycling. As introduced in Chapter 1, LTO exhibits exceptional mechanical robustness and high safety characteristics, primarily due to its unique crystallographic framework and near-zero volumetric variation upon lithium insertion and extraction [1,2].

LTO crystallizes in a cubic spinel structure belonging to the $Fd\bar{3}m$ space group. Within this lattice, lithium ions occupy tetrahedral 8a sites, while titanium ions ($Ti^{4+}$) reside in the octahedral 16d sites, with oxygen atoms located at the 32e positions, forming a close-packed cubic framework. This ordered cation distribution produces a three-dimensional network of $Li^+$ diffusion pathways, facilitating reversible lithium transport within the solid host structure [1,3].

During lithiation, LTO undergoes a reversible two-phase transformation to $Li_7Ti_5O_{12}$. In this process, additional lithium ions occupy previously vacant octahedral 16c sites, while the oxygen sublattice remains essentially unchanged. The structural transition between $Li_4Ti_5O_{12}$ and $Li_7Ti_5O_{12}$ is accompanied by an extremely small lattice variation (≤0.2 %), which classifies LTO as a "zero-strain" anode material [2,4].

As illustrated in Figure 2.1, the crystallographic symmetry of $Li_4Ti_5O_{12}$ remains largely preserved during lithiation and delithiation processes. The preservation of the oxygen framework prevents structural collapse and maintains the integrity of the diffusion network during cycling.

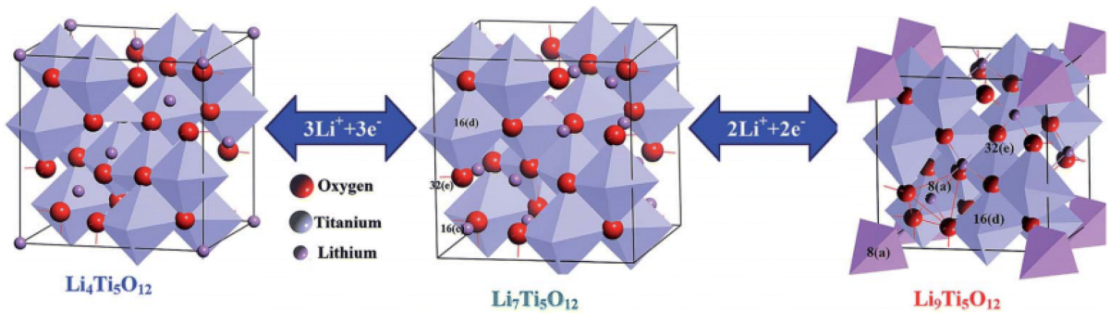



***Figure 2.1111:*** *Schematic representation of the lithiation and delithiation mechanism in spinel $Li_4Ti_5O_{12}$, illustrating lithium insertion into octahedral sites while preserving the oxygen framework and maintaining minimal lattice distortion. Adapted from Wagemaker et al. [5].*

Such structural stability distinguishes $Li_4Ti_5O_{12}$ from many conventional negative electrode materials that undergo substantial lattice expansion and contraction during lithium insertion and extraction. In materials such as silicon, tin, or conversion-type oxides, repeated volumetric fluctuations often lead to particle cracking, electrode

pulverization, and loss of electronic percolation pathways. In contrast, the near-zero strain behavior of LTO significantly suppresses these degradation mechanisms, enabling long-term electrochemical durability [4,5].

From a transport perspective, lithium diffusion in LTO occurs through the three-dimensional spinel framework. Reported ambipolar diffusion coefficients typically range between $10^{-13}$ and $10^{-11}$ $cm^2$ $s^{-1}$, depending on particle size, defect chemistry, porosity, and electrode architecture [11,12]. Although these diffusivity values are generally lower than those reported for graphite-based anodes, the diffusion framework in LTO remains structurally intact over extended cycling due to its near-zero volume change, which preserves lithium transport pathways and minimizes transport degradation [2,4].

Electrochemically, LTO exhibits a highly flat voltage plateau at approximately 1.55 V vs. $Li^+/Li$, corresponding to the $Ti^{4+}/Ti^{3+}$ redox couple during both charge and discharge processes. This plateau reflects a thermodynamically driven two-phase coexistence between $Li_4Ti_5O_{12}$ and $Li_7Ti_5O_{12}$ during lithium insertion and extraction [1,6]. Importantly, the operating potential of LTO remains sufficiently high to suppress lithium metal plating under typical conditions and does not strongly promote reductive decomposition reactions in conventional carbonate-based electrolytes [7].

In aqueous lithium-ion battery (ALIB) systems, however, additional challenges arise due to the hydrogen evolution reaction (HER). When electrode potentials approach sufficiently negative values, proton reduction or water splitting may compete with lithium insertion reactions, generating hydrogen gas and inducing parasitic degradation processes. The competition between lithium insertion and HER at the electrode–electrolyte interface is illustrated schematically in Figure 2.2.

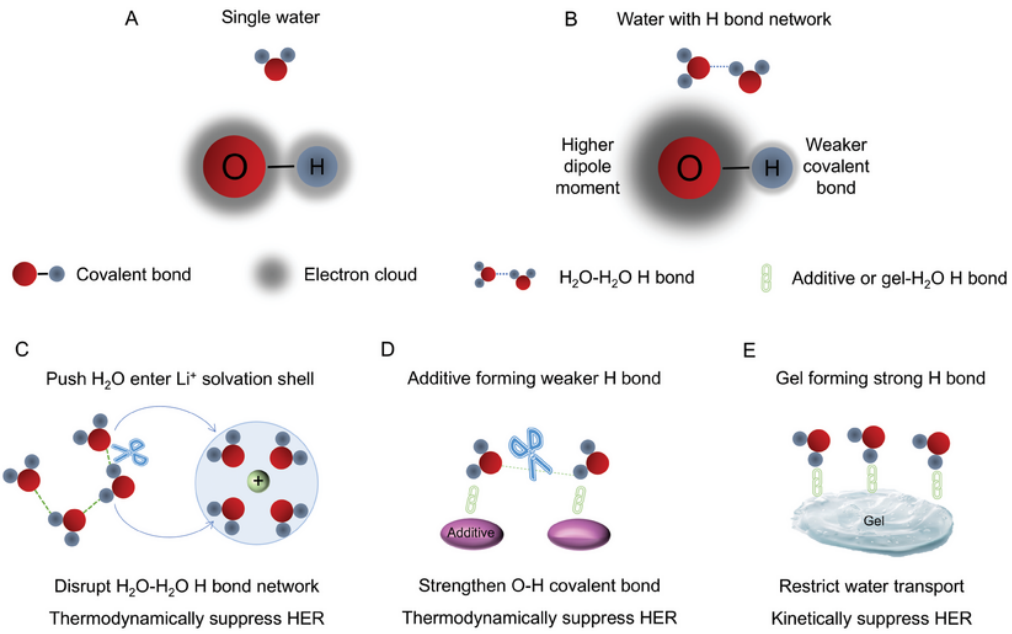



**Figure 2.2222:** Schematic representation of competing electrochemical reactions at the anode–electrolyte interface in aqueous battery systems, highlighting the competition between $Li^+$ insertion and hydrogen evolution reactions (HER). Adapted from Liu et al. *[14].*

As shown in Figure 2.2, hydrogen evolution can occur when proton reduction becomes kinetically favorable relative to lithium insertion. Suppressing this parasitic reaction is therefore essential for achieving stable operation in aqueous electrochemical systems [8]. Interestingly, several studies have reported that LTO exhibits comparatively sluggish HER kinetics relative to carbonaceous electrodes. This behavior has been attributed to the electronic structure of the Ti–O framework, which provides unfavorable adsorption energetics for hydrogen species and therefore limits proton reduction pathways [20].

Because LTO experiences negligible structural degradation during cycling, performance fading in LTO-based systems is often dominated by interfacial reactions rather than mechanical damage of the active material. Consequently, LTO is frequently employed as a model anode material for investigating electrolyte–electrode interfacial phenomena and interphase formation mechanisms [7,10].

Gel polymer electrolytes (GPEs) have also been explored as an alternative strategy for improving interfacial stability in aqueous battery systems. In such electrolytes, polymer networks spatially confine water molecules and solvated ions, thereby reducing proton mobility and limiting parasitic reactions such as hydrogen evolution [38–41]. Although many studies have focused on Zn-based aqueous batteries, the same confinement principles are considered applicable to other insertion-type anodes, including $Li_4Ti_5O_{12}$ [39,41].

To improve the electrochemical stability of aqueous battery systems, extensive research has focused on the development of advanced electrolyte concepts that modify the structure and activity of water molecules [8,34–37]. As illustrated in Figure 2.3, several electrolyte engineering strategies have been proposed, including dilute and concentrated aqueous electrolytes, water-in-salt electrolytes, and deep eutectic solvent formulations. These approaches aim to regulate ion solvation structures, reduce the activity of free water molecules, and suppress parasitic reactions such as hydrogen evolution [8,35,37].

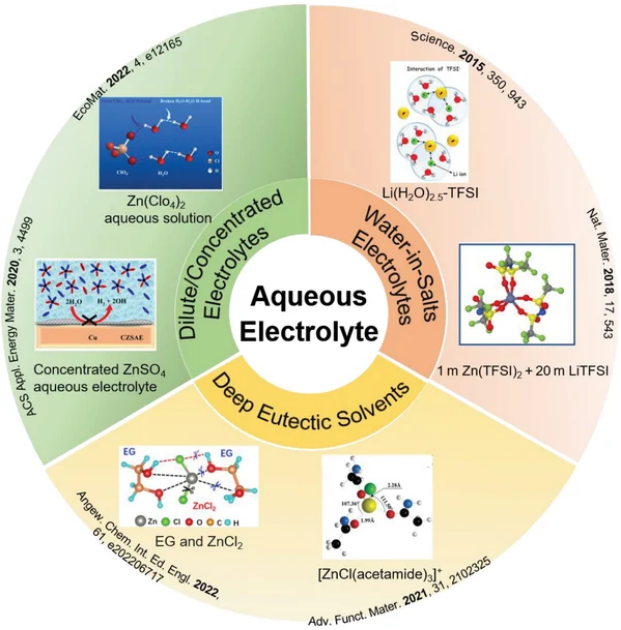



**Figure 2.3333:** Overview of electrolyte engineering strategies for aqueous electrochemical energy storage systems, including dilute and concentrated aqueous electrolytes, water-in-salt electrolytes, and deep eutectic solvent systems. These approaches modify ion solvation structures and reduce the activity of free water molecules, thereby extending the electrochemical stability window of aqueous batteries *[38-41]*.

Among these strategies, water-in-salt electrolytes (WiSE) have attracted particular attention because the high salt concentration significantly alters the $Li^+$ solvation environment. In such systems, most water molecules become coordinated to lithium ions, reducing the fraction of uncoordinated water molecules that can participate in parasitic electrochemical reactions. The modification of $Li^+$ solvation structures in highly concentrated electrolytes is illustrated schematically in Figure 2.4.

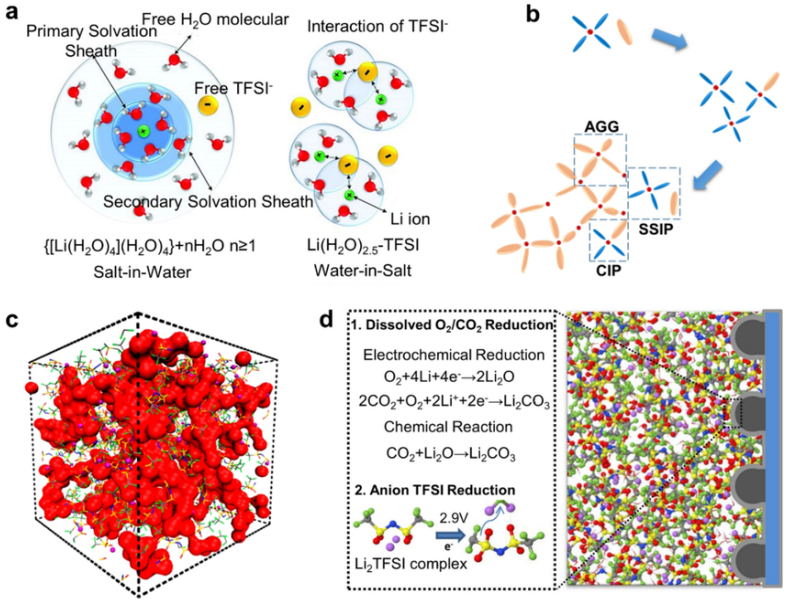



***Figure 2.4444:*** *Comparison of $Li^+$ solvation structures in dilute aqueous electrolytes and water-in-salt electrolytes, illustrating the reduction of free water molecules and the formation of an anion-rich solvation environment at high salt concentrations. Adapted from Suo et al. [8].*

As shown in Figure 2.4, the altered solvation structure significantly reduces the activity of free water molecules and therefore suppresses hydrogen evolution reactions, allowing the practical electrochemical stability window of aqueous batteries to extend well beyond the thermodynamic decomposition limit of water (~1.23 V) [8,35].

Taken together, the literature reviewed in this section highlights the unique role of LTO as a structurally stable and electrochemically robust anode material for aqueous lithium-ion batteries. Its combination of zero-strain lithiation behavior, relatively sluggish HER kinetics, and compatibility with advanced electrolyte engineering strategies makes LTO an ideal platform for investigating electrolyte–electrode interfacial processes and developing safer aqueous energy storage systems [1,4].

## 2.2 Comparison with other Anodes

Among titanium-based insertion hosts, $TiO_2$ polymorphs are most frequently compared with LTO due to their shared Ti-based redox chemistry, yet their performance in aqueous batteries differs substantially as a result of differences in lithiation strain, surface evolution, and HER susceptibility [3, 4]. Anatase $TiO_2$ exhibits a higher theoretical capacity (~335 mAh $g^{-1}$) compared with LTO (~175 mAh $g^{-1}$); however, studies on $TiO_2$ insertion mechanisms have shown that anatase undergoes more pronounced structural distortion and surface evolution during cycling, particularly under conditions involving deep lithiation or aqueous environments [5, 27]. Under aqueous polarization, proton co-insertion and hydrated-ion interactions may further promote defect formation and surface reconstruction, increasing catalytic activity toward hydrogen evolution and leading to gas evolution, impedance growth, and reduced Coulombic efficiency over prolonged cycling [27, 30]. In contrast, LTO's near-zero strain lithiation suppresses mechanically driven surface reactivation, helping to maintain a more stable electrode–electrolyte interface and improved cycling stability over extended operation [1, 4].

Aqueous compatibility has also been explored for $TiO_2$ bronze-type phases, commonly denoted $TiO_2$ (B). $TiO_2$ (B) is a monoclinic polymorph characterized by an open-channel framework that facilitates $Li^+$ diffusion and generally exhibits reduced volume-change severity relative to anatase [4, 5]. Nevertheless, even in $TiO_2$ (B), hydrogen evolution can still be activated at defect-rich regions and edge terminations, particularly as partial surface reconstruction develops during deep cycling in aqueous environments [27, 30]. Overall, these findings suggest that while $TiO_2$-based anodes can exhibit higher initial capacity, LTO provides superior long-term aqueous stability because its performance is less affected by strain-driven aging and interfacial catalytic evolution [1, 21, 45].

NASICON-type titanates and related phosphate frameworks (e.g., $NaTi_2(PO_4)_3$ and structurally analogous compounds) are also considered attractive for aqueous batteries

due to their robust three-dimensional frameworks and favorable ionic transport characteristics. However, Wu et al. demonstrated that their practical aqueous operation often requires more extensive electrolyte and interphase engineering to suppress hydrogen evolution reactions (HER) and maintain stable cycling performance, including strategies such as pH buffering, concentrated electrolyte concepts, and interfacial modification approaches [47]. In aqueous media, where the limiting factor is frequently parasitic reaction control rather than purely capacity-driven metrics, LTO remains advantageous due to its structurally stable insertion mechanism and its comparatively consistent interfacial response under prolonged cycling [1, 20, 22].

Performance differences become more pronounced when LTO is compared with conversion-type anodes (e.g., $Fe_3O_4$, $Mn_3O_4$, $MoS_2$), which can deliver high initial capacities but inherently involve bond-breaking and bond-forming reactions that drive large structural rearrangements during cycling [24]. Such conversion processes generate evolving phase boundaries, volume-change-induced cracking, and continuous surface reconfiguration, which in aqueous electrolytes can further accelerate corrosion and dissolution pathways and promote unstable Coulombic efficiency [24, 28]. While nanostructuring and carbon encapsulation may partially mitigate these effects, these strategies can simultaneously increase the number of electrochemically active surface sites, potentially enhance HER kinetics and complicate interfacial chemistry [30]. In contrast, LTO's insertion-only mechanism maintains a stable geometrical and electronic interface, reducing the likelihood of progressive catalytic activation and enabling significantly improved cycle retention under similar aqueous conditions [1, 22, 28].

A comparative summary of representative anode families under aqueous-relevant constraints is provided in Table 2.1, highlighting that the "best" anode in aqueous batteries is not necessarily the one with the highest theoretical capacity, but rather the one offering the most balanced combination of mechanical stability, interfacial robustness, HER tolerance, and sustained cycling performance [28]. While $TiO_2$ polymorphs and conversion-type anodes may exhibit higher initial capacities, they are generally more susceptible to strain-driven degradation and progressive interfacial activation [5, 22, 28, 32]. NASICON-type anodes provide favorable transport properties but often require substantial electrolyte/interphase engineering to remain stable near HER-limited conditions [47]. In contrast, LTO combines a structurally invariant insertion framework with inherently stable cycling behavior, making it one of the most practically viable and mechanistically informative negative electrodes for aqueous battery research and long-duration stationary operation [1, 4, 22, 28].

| Anode material | Representative materials | Charge mechanism | Key structural feature | Main Advantages in aqueous | Main limitation in aqueous media | Typical mitigation strategies | Ref. |
|---|---|---|---|---|---|---|---|
| **LTO** | $Li_4Ti_5O_{12}$ (LTO) | Insertion ($Ti^{4+}/Ti^{3+}$) | Cubic spinel, zero-strain lithiation | Excellent cycling stability, strong mechanical integrity, stable interphase behavior; suitable baseline for mechanistic studies | Low intrinsic electronic conductivity: performance depends on $Li^+/H^+$ interfacial selectivity | Conductive carbon composites; electrode architecture optimization; water-activity control (WiSE/LHCE); gel confinement | [1, 4, 22, 28] |
| **$TiO_2$ polymorphs** | Anatase $TiO_2$, $TiO_2$(B) | Insertion / mixed | Anatase: tetragonal; $TiO_2$(B): monoclinic open-channel | Higher theoretical capacity vs LTO; $TiO_2$(B) improved diffusion | Lattice distortion and surface reconstruction; defect-driven HER activation | Electrolyte engineering; surface coatings; controlled nanostructuring | [5, 22, 28, 32] |
| **NASICON** | $NaTi_2(PO_4)_3$ | Insertion | 3D polyanionic framework | High ionic conductivity; stable framework | HER competition; interphase sensitivity | pH buffering; interphase modification; concentrated electrolytes | [28, 47] |
| **Conversion anodes** | $Fe_3O_4$, $Mn_3O_4$, $MoS_2$ | Conversion | Phase transformation reactions | Very high initial capacity | Volume change, dissolution, unstable interphase, gas evolution | Carbon encapsulation; nanostructuring; electrolyte stabilization | [28, 32] |
| **Carbon anodes** | Graphite, porous carbons | Insertion / adsorption | Layered or porous network | High electronic conductivity; mature processing | Thermodynamic instability vs HER in water | High-concentration electrolytes; coatings; gel confinement | [20, 28, 46] |

***Table 2.1111:*** *Comparison of representative negative-electrode materials for aqueous lithium-ion batteries (ALIBs) under HER-limited conditions*

As highlighted in Table 2.1, LTO provides the most balanced performance profile for aqueous operation due to its zero-strain insertion mechanism and stable interfacial response, whereas $TiO_2$ polymorphs and conversion-type anodes often experience progressive surface evolution and increased HER activity during cycling. Consequently, electrolyte strategies such as water-activity control and gel confinement are particularly effective when combined with structurally invariant insertion hosts such as LTO.

Taken together, the comparative analysis presented above clarifies the rationale for selecting $Li_4Ti_5O_{12}$ as the model anode material in ALIB research. Unlike $TiO_2$ polymorphs, which suffer from strain-induced surface evolution and progressive catalytic activation toward hydrogen evolution, and conversion-type materials that undergo large structural rearrangements and interfacial instability, LTO combines structural invariance with electrochemical robustness [4, 24, 28]. Its zero-strain

lithiation mechanism minimizes mechanical degradation, while its spinel framework provides stable three-dimensional $Li^+$ diffusion pathways that remain preserved during long-term cycling [1, 6, 11]. In addition, LTO can be synthesized through scalable and compositionally tunable routes, allowing flexible modification via doping, surface coatings, and electrode-architecture engineering without compromising structural integrity [4, 17, 18, 22]. Consequently, the primary limitations in LTO coupled with aqueous electrolytes arise not from intrinsic material instability but from electrolyte–interphase interactions, making LTO an ideal platform for mechanistic investigations aimed at decoupling interfacial chemistry from bulk degradation effects [7, 29, 33]. For these reasons, LTO serves as a particularly suitable reference anode for evaluating stabilization strategies in ALIBs, forming the foundation for the analysis developed in the following section [10, 22, 28].

## 2.3 Enhancing LTO Stability

Operando characterization techniques have become increasingly important for understanding interfacial processes occurring in aqueous battery systems. Methods such as floating potential spectroscopy, operando Raman spectroscopy, and quantitative gas-evolution analysis enable direct monitoring of electrochemical reactions occurring at electrode surfaces during battery operation. These approaches provide valuable insight into parasitic reactions such as hydrogen evolution, which may compete with lithium insertion processes in aqueous environments [32,33,45].

Operando experiments have confirmed that hydrogen evolution at LTO electrodes in neutral sulfate electrolytes may initiate at potentials more negative than those predicted by simplified thermodynamic considerations but typically requires substantial kinetic overpotentials for nucleation [32,33,45]. Importantly, Chen et al. demonstrated that the zero-strain insertion mechanism of LTO suppresses microcracking and limits the continuous exposure of fresh catalytic sites during cycling, thereby preventing progressive activation of hydrogen evolution with aging [22]. This behavior contrasts with many alternative anode materials whose catalytic activity toward hydrogen evolution increases as cycling-induced structural changes expose additional reactive surface sites [28,32].

The experimental configurations used for operando monitoring of electrochemical reactions are illustrated in Figure 2.5. Such setups allow real-time observation of interfacial processes during electrochemical cycling.

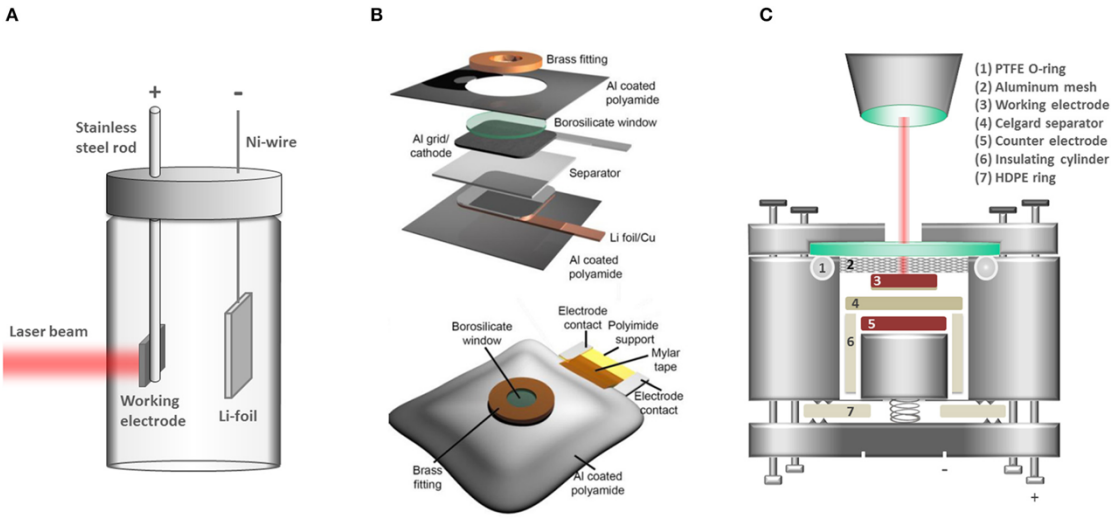



***Figure 2.5555:*** *Representative operando Spectro electrochemical cell configurations used for in-situ investigation of battery electrodes. (A) Electrochemical cell designed for operando Raman spectroscopy, where a laser beam probes the working electrode during electrochemical cycling. (B) Exploded view of an operando Spectro electrochemical cell enabling optical access through a borosilicate window. (C) Cross-section of an operando cell used for laser-based characterization of electrode processes. These configurations allow real-time monitoring of interfacial reactions such as gas evolution and surface chemistry changes during battery operation. Adapted from operando battery spectroscopy studies [32,33,45].*

As illustrated in Figure 2.5, operando techniques provide simultaneous information on electrochemical performance and interfacial chemical evolution during battery operation. Such approaches have been widely used to monitor gas evolution, electrolyte decomposition, and surface chemistry changes during cycling, providing valuable insight into degradation mechanisms in lithium-ion and aqueous battery systems. Real-time spectroscopic techniques are particularly useful for identifying competing reactions such as hydrogen evolution and electrolyte decomposition at electrode surfaces [32,33,45].

Electrolyte engineering provides an additional pathway for stabilizing aqueous battery systems. Suo et al. reported that increasing salt concentration alters the $Li^+$ solvation environment and reduces the fraction of uncoordinated water molecules, thereby kinetically suppressing hydrogen evolution reactions [8]. Borodin et al. further demonstrated that such solvation-driven effects can expand the practical electrochemical stability window beyond the classical thermodynamic decomposition limit of 1.23 V characteristic of dilute aqueous electrolytes [35]. In LTO-based cells, these electrolyte modifications synergize with the mechanically stable insertion framework of LTO, allowing operation closer to the $Ti^{4+}/Ti^{3+}$ redox regime while reducing gas evolution and impedance growth compared with more dynamically evolving anodes [22,28,36].

A complementary strategy involves the use of gel polymer electrolytes (GPEs) and hydrogel-type electrolyte matrices. In these systems, polymer networks immobilize a liquid electrolyte phase while maintaining ionic conductivity. This architecture spatially confines water molecules and solvated ions, thereby reducing proton mobility and limiting parasitic reactions such as hydrogen evolution [38–41]. Such polymer-confined electrolytes can provide improved mechanical stability at the electrode–electrolyte interface while preserving efficient ion transport pathways. The concept of

electrolyte confinement and ion transport in gel polymer systems is illustrated in Figure 2.6.

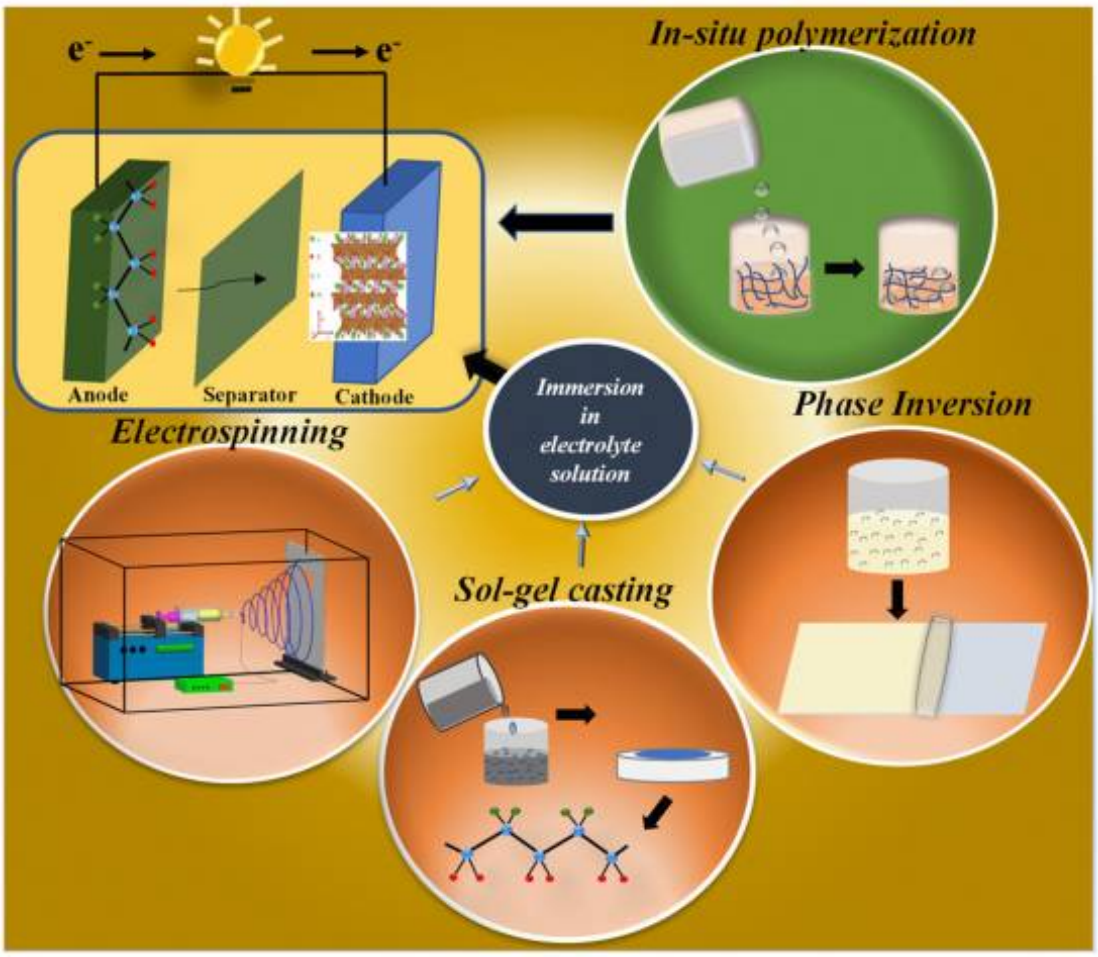



***Figure 2.6666:*** *Conceptual representation of electrochemical operation in polymer-based electrolyte systems. The electrode is immersed in an electrolyte environment in which ion transport occurs through a polymer-confined electrolyte phase. The polymer network spatially restricts solvent mobility while maintaining ionic conductivity, thereby stabilizing the electrode–electrolyte interface and reducing parasitic reactions such as hydrogen evolution. Adapted from recent studies on gel polymer electrolytes for rechargeable batteries [38–41].*

ollectively, the mechanistic insights discussed in this chapter demonstrate that the electrochemical performance of LTO in aqueous systems is governed by the interplay between structural stability, electrolyte chemistry, and interfacial regulation rather than by intrinsic capacity alone. These findings provide the conceptual framework for the experimental approach adopted in this thesis, where electrode synthesis routes and architecture design are tailored to exploit the zero-strain characteristics and interfacial stability of LTO-based systems. Accordingly, the following chapters focus on the synthesis methodology, material processing, and electrochemical evaluation strategies developed to translate these literature-derived principles into practical electrode configurations, as presented in Chapters 3 and 4.

## 2.4 References


[1] T. Ohzuku, A. Ueda, and N. Yamamoto, “Zero-Strain Insertion Material of Li [ Li1 / 3Ti5 / 3 ] O 4 for Rechargeable Lithium Cells,” J. Electrochem. Soc., vol. 142, no. 5, pp. 1431–1435, May 1995, doi: 10.1149/1.2048592.

[2] K. Zaghib, M. Simoneau, M. Armand, and M. Gauthier, “Electrochemical study of Li4Ti5O12 as negative electrode for Li-ion polymer rechargeable batteries,” J. Power Sources, vol. 81–82, pp. 300–305, Sep. 1999, doi: 10.1016/S0378-7753(99)00209-8.

[3] J. B. Goodenough and Y. Kim, “Challenges for Rechargeable Li Batteries,” Chem. Mater., vol. 22, no. 3, pp. 587–603, Feb. 2010, doi: 10.1021/cm901452z.

[4] 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,” Ceram. Int., vol. 47, no. 5, pp. 5870–5895, Mar. 2021, doi: 10.1016/j.ceramint.2020.10.241.

[5] M. Wagemaker, W. J. H. Borghols, and F. M. Mulder, “Large Impact of Particle Size on Insertion Reactions. A Case for Anatase $Li_x TiO_2$,” J. Am. Chem. Soc., vol. 129, no. 14, pp. 4323–4327, Apr. 2007, doi: 10.1021/ja067733p.

[6] L. Aldon et al., “Chemical and Electrochemical Li-Insertion into the $Li_4 Ti_5 O_{12}$ Spinel,” Chem. Mater., vol. 16, no. 26, pp. 5721–5725, Dec. 2004, doi: 10.1021/cm0488837.

[7] K. Xu, “Nonaqueous Liquid Electrolytes for Lithium-Based Rechargeable Batteries,” Chem. Rev., vol. 104, no. 10, pp. 4303–4418, Oct. 2004, doi: 10.1021/cr030203g.

[8] L. Suo et al., "'Water-in-salt' electrolyte enables high-voltage aqueous lithium-ion chemistries," Science, vol. 350, no. 6263, pp. 938–943, Nov. 2015, doi: 10.1126/science.aab1595.
[9] T. Ohzuku and Y. Makimura, "Layered Lithium Insertion Material of LiCo1/3Ni1/3Mn1/3O2 for Lithium-Ion Batteries," Chem. Lett., vol. 30, no. 7, pp. 642–643, Jul. 2001, doi: 10.1246/cl.2001.642.
[10] M. R. Palacín, "Recent advances in rechargeable battery materials: a chemist's perspective," Chem. Soc. Rev., vol. 38, no. 9, p. 2565, 2009, doi: 10.1039/b820555h.
[11] M. Wagemaker, E. R. H. Van Eck, A. P. M. Kentgens, and F. M. Mulder, "Li-Ion Diffusion in the Equilibrium Nanomorphology of Spinel $Li_{4+x}Ti_5O_{12}$," J. Phys. Chem. B, vol. 113, no. 1, pp. 224–230, Jan. 2009, doi: 10.1021/jp8073706.
[12] Y. H. Rho and K. Kanamura, "Li+ ion diffusion in Li4Ti5O12 thin film electrode prepared by PVP sol–gel method," J. Solid State Chem., vol. 177, no. 6, pp. 2094–2100, Jun. 2004, doi: 10.1016/j.jssc.2004.02.018.
[13] C. Jiang, M. Ichihara, I. Honma, and H. Zhou, "Effect of particle dispersion on high rate performance of nano-sized Li4Ti5O12 anode," Electrochimica Acta, vol. 52, no. 23, pp. 6470–6475, Jul. 2007, doi: 10.1016/j.electacta.2007.04.070.
[14] W. Liu et al., "Mesoporous Spinel Li4Ti5O12 Nanoparticles for High Rate Lithium-ion Battery Anodes," Electrochimica Acta, vol. 133, pp. 578–582, Jul. 2014, doi: 10.1016/j.electacta.2014.04.072.
[15] Y. Tang, F. Huang, W. Zhao, Z. Liu, and D. Wan, "Synthesis of graphene-supported Li4Ti5O12 nanosheets for high rate battery application," J. Mater. Chem., vol. 22, no. 22, p. 11257, 2012, doi: 10.1039/c2jm30624g.
[16] J.-H. Choi et al., "Multi-layer electrode with nano-Li4Ti5O12 aggregates sandwiched between carbon nanotube and graphene networks for high power Li-ion batteries," Sci. Rep., vol. 4, no. 1, p. 7334, Dec. 2014, doi: 10.1038/srep07334.
[17] B. Tian, H. Xiang, L. Zhang, Z. Li, and H. Wang, "Niobium doped lithium titanate as a high rate anode material for Li-ion batteries," Electrochimica Acta, vol. 55, no. 19, pp. 5453–5458, Jul. 2010, doi: 10.1016/j.electacta.2010.04.068.
[18] J. Kim et al., "$Zr^{4+}$ Doping in $Li_4Ti_5O_{12}$ 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.
[19] H. Zhao, Y. Li, Z. Zhu, J. Lin, Z. Tian, and R. Wang, "Structural and electrochemical characteristics of Li4−Al Ti5O12 as anode material for lithium-ion batteries," Electrochimica Acta, vol. 53, no. 24, pp. 7079–7083, Oct. 2008, doi: 10.1016/j.electacta.2008.05.038.
[20] W. Li, J. R. Dahn, and D. S. Wainwright, "Rechargeable Lithium Batteries with Aqueous Electrolytes," Science, vol. 264, no. 5162, pp. 1115–1118, May 1994, doi: 10.1126/science.264.5162.1115.
[21] J. Li, R. B. Lewis, and J. R. Dahn, "Sodium Carboxymethyl Cellulose," Electrochem. Solid-State Lett., vol. 10, no. 2, p. A17, 2007, doi: 10.1149/1.2398725.
[22] Z. Chen, I. Belharouak, Y. -K. Sun, and K. Amine, "Titanium-Based Anode Materials for Safe Lithium-Ion Batteries," Adv. Funct. Mater., vol. 23, no. 8, pp. 959–969, Feb. 2013, doi: 10.1002/adfm.201200698.
[23] J. B. Goodenough and K.-S. Park, "The Li-Ion Rechargeable Battery: A Perspective," J. Am. Chem. Soc., vol. 135, no. 4, pp. 1167–1176, Jan. 2013, doi: 10.1021/ja3091438.

[24] M. N. Obrovac and V. L. Chevrier, “Alloy Negative Electrodes for Li-Ion Batteries,” Chem. Rev., vol. 114, no. 23, pp. 11444–11502, Dec. 2014, doi: 10.1021/cr500207g.
[25] S. Chen et al., “High-Voltage Lithium-Metal Batteries Enabled by Localized High-Concentration Electrolytes,” Adv. Mater., vol. 30, no. 21, p. 1706102, May 2018, doi: 10.1002/adma.201706102.
[26] U. Kasavajjula, C. Wang, and A. J. Appleby, “Nano- and bulk-silicon-based insertion anodes for lithium-ion secondary cells,” J. Power Sources, vol. 163, no. 2, pp. 1003–1039, Jan. 2007, doi: 10.1016/j.jpowsour.2006.09.084.
[27] J. Cho, Y. J. Kim, and B. Park, “Novel $LiCoO_2$ Cathode Material with $Al_2 O_3$ Coating for a Li Ion Cell,” Chem. Mater., vol. 12, no. 12, pp. 3788–3791, Dec. 2000, doi: 10.1021/cm000511k.
[28] D. Chao et al., “Roadmap for advanced aqueous batteries: From design of materials to applications,” Sci. Adv., vol. 6, no. 21, p. eaba4098, May 2020, doi: 10.1126/sciadv.aba4098.
[29] J. K. Nørskov, T. Bligaard, J. Rossmeisl, and C. H. Christensen, “Towards the computational design of solid catalysts,” Nat. Chem., vol. 1, no. 1, pp. 37–46, Apr. 2009, doi: 10.1038/nchem.121.
[30] Y. Zheng, Y. Jiao, M. Jaroniec, and S. Z. Qiao, “Advancing the Electrochemistry of the Hydrogen-Evolution Reaction through Combining Experiment and Theory,” Angew. Chem. Int. Ed., vol. 54, no. 1, pp. 52–65, Jan. 2015, doi: 10.1002/anie.201407031.
[31] D. Voiry et al., “Best Practices for Reporting Electrocatalytic Performance of Nanomaterials,” ACS Nano, vol. 12, no. 10, pp. 9635–9638, Oct. 2018, doi: 10.1021/acsnano.8b07700.
[32] N. Dubouis and A. Grimaud, “The hydrogen evolution reaction: from material to interfacial descriptors,” Chem. Sci., vol. 10, no. 40, pp. 9165–9181, 2019, doi: 10.1039/C9SC03831K.
[33] J. Maibach, J. Rizell, A. Matic, and N. Mozhzhukhina, “Toward Operando Characterization of Interphases in Batteries,” ACS Mater. Lett., vol. 5, no. 9, pp. 2431–2444, Sep. 2023, doi: 10.1021/acsmaterialslett.3c00207.
[34] L. Suo et al., “Advanced High-Voltage Aqueous Lithium-Ion Battery Enabled by ‘Water-in-Bisalt’ Electrolyte,” Angew. Chem. Int. Ed., vol. 55, no. 25, pp. 7136–7141, Jun. 2016, doi: 10.1002/anie.201602397.
[35] O. Borodin, J. Self, K. A. Persson, C. Wang, and K. Xu, “Uncharted Waters: Super-Concentrated Electrolytes,” Joule, vol. 4, no. 1, pp. 69–100, Jan. 2020, doi: 10.1016/j.joule.2019.12.007.
[36] L. Chen et al., “A 63 m Superconcentrated Aqueous Electrolyte for High-Energy Li-Ion Batteries,” ACS Energy Lett., vol. 5, no. 3, pp. 968–974, Mar. 2020, doi: 10.1021/acsenergylett.0c00348.
[37] R.-S. Kühnel, D. Reber, A. Remhof, R. Figi, D. Bleiner, and C. Battaglia, “‘Water-in-salt’ electrolytes enable the use of cost-effective aluminum current collectors for aqueous high-voltage batteries,” Chem. Commun., vol. 52, no. 68, pp. 10435–10438, 2016, doi: 10.1039/C6CC03969C.
[38] Z. Wang et al., “Hydrogel Electrolytes for Flexible Aqueous Energy Storage Devices,” Adv. Funct. Mater., vol. 28, no. 48, p. 1804560, Nov. 2018, doi: 10.1002/adfm.201804560.
[39] H. Wang et al., “Concentrated Hydrogel Electrolyte-Enabled Aqueous Rechargeable NiCo//Zn Battery Working from −20 to 50 °C,” ACS Appl. Mater. Interfaces, vol. 11, no. 1, pp. 49–55, Jan. 2019, doi: 10.1021/acsami.8b18003.

[40] T. K. L. Nguyen and T.-N. Pham-Truong, “Recent Advancements in Gel Polymer Electrolytes for Flexible Energy Storage Applications,” Polymers, vol. 16, no. 17, p. 2506, Sep. 2024, doi: 10.3390/polym16172506.
[41] Z. Tian, P. He, and A. Toor, “Development of deformable aqueous Li-ion batteries enabled by water-in-salt-based hydrogel electrolytes,” Nano Energy, vol. 148, p. 111617, Feb. 2026, doi: 10.1016/j.nanoen.2025.111617.
[42] Z. Wang et al., “Hydrogel Electrolytes for Flexible Aqueous Energy Storage Devices,” Adv. Funct. Mater., vol. 28, no. 48, p. 1804560, Nov. 2018, doi: 10.1002/adfm.201804560.
[43] C. Y. Chan, Z. Wang, H. Jia, P. F. Ng, L. Chow, and B. Fei, “Recent advances of hydrogel electrolytes in flexible energy storage devices,” J. Mater. Chem. A, vol. 9, no. 4, pp. 2043–2069, 2021, doi: 10.1039/D0TA09500A.
[44] Y.-J. Zhang, Q. Ye, and M. Ni, “The impact of in-situ hydrogen evolution on the flow resistance of electrolyte flowing through the carbon felt electrode in a redox flow battery,” J. Power Sources, vol. 564, p. 232837, Apr. 2023, doi: 10.1016/j.jpowsour.2023.232837.
[45] X. Hou, L. Zhang, N. Gogoi, K. Edström, and E. J. Berg, “Interfacial Chemistry in Aqueous Lithium-Ion Batteries: A Case Study of $V_2$ $O_5$ in Dilute Aqueous Electrolytes,” Small, vol. 20, no. 23, p. 2308577, Jun. 2024, doi: 10.1002/smll.202308577.
[46] P. Simon and Y. Gogotsi, “Materials for electrochemical capacitors,” Nat. Mater., vol. 7, no. 11, pp. 845–854, Nov. 2008, doi: 10.1038/nmat2297.
[47] M. Wu, W. Ni, J. Hu, and J. Ma, “NASICON-Structured NaTi2(PO4)3 for Sustainable Energy Storage,” Nano-Micro Lett., vol. 11, no. 1, p. 44, Dec. 2019, doi: 10.1007/s40820-019-0273-1.

# 3. Synthesis Methods of LTO

## 3.1 Purpose of the Synthesis

The synthesis of $Li_4Ti_5O_{12}$ is primarily driven by the need to optimize structural and functional properties beyond those typically achieved in commercially available powders. Although LTO is intrinsically known for its zero-strain lithiation mechanism, its electrochemical performance is strongly governed by synthesis-dependent parameters rather than by crystal structure alone, as first demonstrated by Ohzuku et al. [1]. Commercial LTO materials often exhibit particle sizes exceeding 1 µm, which increase lithium diffusion pathways, reduce the effective electrode–electrolyte interfacial area, and enhance parasitic polarization during high-rate operation, as discussed in studies of LTO electrochemistry by Yi et al. [2]. These effects become particularly critical in aqueous electrolytes, where the narrow electrochemical stability window of water amplifies the importance of interfacial kinetics and ion transport.

LTO is further characterized by intrinsically low electronic conductivity, typically reported in the range of $10^{-13}$–$10^{-9}$ S $cm^{-1}$, resulting in high charge-transfer resistance and limited high-rate lithium intercalation [2]. However, literature reports consistently demonstrate that this limitation arises largely from microstructural and surface characteristics imposed by synthesis conditions rather than from the spinel framework itself. For example, Yi et al. [2] showed that improved crystallinity and optimized particle morphology significantly reduce polarization and enhance electrochemical utilization of LTO. Similarly, Julien et al. [3] reported that particle-size reduction and conductive carbon integration markedly improve electronic percolation, capacity retention, and rate capability in liquid electrolyte systems.

Phase purity constitutes an additional critical aspect of LTO synthesis. Minor deviations in stoichiometry or the presence of secondary phases, such as anatase or rutile $TiO_2$, can substantially alter electrochemical behavior. In particular, anatase $TiO_2$ undergoes electrochemical reactions within potential regions overlapping with the onset of aqueous hydrogen evolution, thereby promoting parasitic reactions and accelerating electrode degradation, as discussed in studies of titanium oxide electrochemistry by Chen and Mao [4]. Achieving high phase purity is therefore essential for ensuring reliable operation under aqueous conditions.

Beyond electrochemical considerations, synthesis optimization aligns with broader objectives related to sustainability, energy consumption, and scalability. Low-temperature chemical routes such as sol–gel and hydrothermal synthesis offer reduced energy input and enhanced control over particle morphology compared with solid-state methods, whereas solid-state synthesis remains attractive for industrial scalability [2]. Balancing electrochemical performance against processing cost, complexity, and environmental footprint therefore represents a central design consideration for LTO materials intended for ALIB applications.

## 3.2 Synthesis Methods

The synthesis route of $Li_4Ti_5O_{12}$ critically governs its microstructural characteristics, including particle size, crystallinity, phase purity, surface chemistry, and defect density, all of which directly influence electrochemical behavior in aqueous lithium-ion systems. Three principal synthesis strategies dominate the literature: sol–gel synthesis, hydrothermal synthesis, and solid-state reaction.

### 3.2.1 Sol–gel synthesis

Sol–gel synthesis is widely regarded as one of the most effective routes for producing nanoscale and compositionally homogeneous $Li_4Ti_5O_{12}$. Its principal advantage lies in near-molecular-level mixing of lithium and titanium precursors prior to gelation, enabling uniform spinel phase formation at relatively low calcination temperatures (typically 600–700 °C) [5]. Such synthesis conditions typically yield LTO particles in the 50–200 nm size range, substantially smaller than those obtained through conventional solid-state synthesis, where particle sizes frequently exceed 1 μm [2,5].

Citrate-assisted sol–gel systems are particularly effective because citric acid stabilizes metal–citrate complexes and suppresses premature precipitation of titanium species. Wang et al. [5] reported that citric-acid-assisted sol–gel synthesis produced phase-pure LTO nanoparticles with average particle sizes of approximately 80–150 nm, significantly smaller than those obtained through conventional solid-state synthesis routes. The reduced particle size and improved precursor homogeneity resulted in enhanced electrochemical performance due to shorter $Li^+$ diffusion pathways and improved electrode–electrolyte contact.

Further improvements in microstructural control have been demonstrated using modified sol–gel approaches incorporating polymeric complexation agents. Zhang et al. [6] employed a citric-acid-based polymerized complex method and obtained phase-pure LTO nanoparticles with sizes typically in the 100–200 nm range after calcination at moderate temperatures. The improved crystallinity and uniform particle morphology achieved through this route contributed to reduced polarization and improved electrochemical utilization of the active material.

Additional control over particle morphology and aggregation can be achieved through the use of structure-directing additives such as polyethylene glycol (PEG). PEG acts as a soft template that inhibits particle coalescence during calcination and promotes the formation of more uniform nanoscale particles. Zhang et al. [7] reported that PEG-assisted sol–gel synthesis produced LTO nanoparticles with particle sizes as small as 50–100 nm, accompanied by narrower particle-size distributions and reduced agglomeration compared with conventional sol–gel synthesis. Electrochemical measurements showed improved rate capability and enhanced capacity retention, which were attributed to the improved microstructural uniformity and increased electrochemically accessible surface area of the PEG-modified materials.

As a result of these synthesis strategies, sol–gel-derived LTO typically exhibits particle sizes in the 50–200 nm range, which is especially advantageous for aqueous lithium-ion battery systems due to shortened $Li^+$ diffusion lengths and increased electrode–electrolyte contact area [5–7].

Figure 3.1 schematically illustrates the general sol–gel synthesis pathway, including precursor dissolution, hydrolysis and polymerization reactions, gel formation, drying into a xerogel, and final calcination leading to nanoparticle formation.

Overall, the sol–gel approach enables homogeneous precursor distribution at the molecular level, which promotes phase-pure LTO formation at lower calcination temperatures compared with conventional solid-state synthesis [5,6]. The resulting nanoscale particles and improved microstructural control contribute to enhanced lithium diffusion kinetics and improved electrochemical performance in aqueous lithium-ion battery systems.

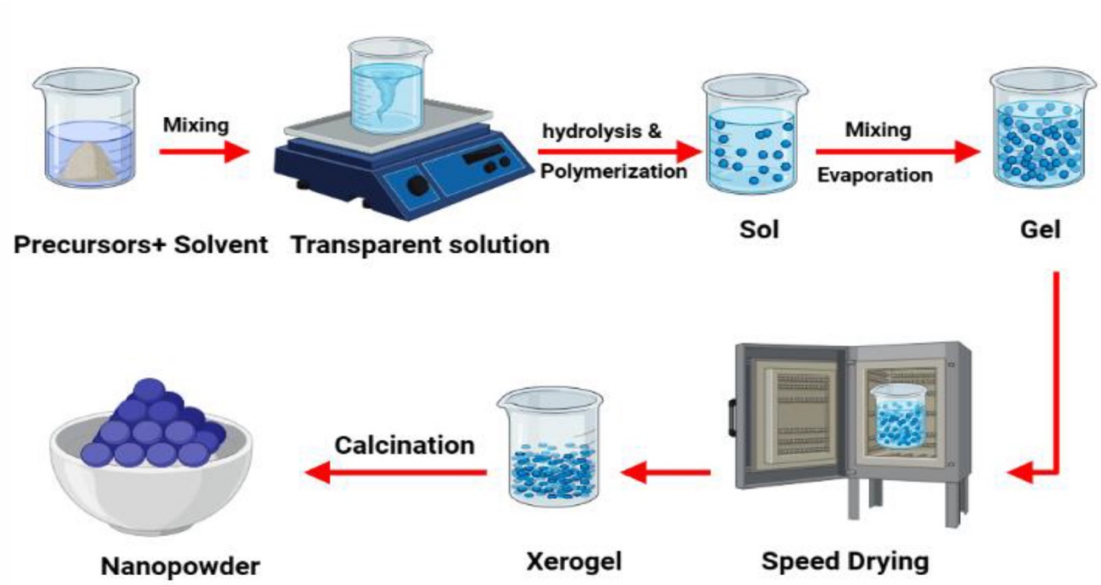



***Figure 3.1111:*** *Schematic illustration of the sol–gel synthesis process. Adapted from Wang et al. [5]*

### 3.2.2 Hydrothermal synthesis

Hydrothermal synthesis represents an alternative wet-chemical route capable of producing highly crystalline $Li_4Ti_5O_{12}$ with controlled morphologies such as nanorods, nanosheets, and hierarchical architectures. Crystallization under elevated temperature and pressure enables controlled nucleation and crystal growth without the extremely high calcination temperatures typically required in solid-state synthesis. For example, Wu et al. [8] demonstrated the hydrothermal synthesis of $Li_4Ti_5O_{12}$ nanosheets followed by moderate heat treatment, yielding highly crystalline materials that exhibited excellent rate capability due to shortened $Li^+$ diffusion pathways. Similarly, Jiang et al. [9] reported hierarchical $Li_4Ti_5O_{12}/TiO_2$ composite tubes prepared through a hydrothermal approach, where the controlled nanostructure improved lithium-ion transport and cycling stability. Χρειάζεται να βάλεις σχήμα με τα tubes

However, hydrothermal synthesis is inherently limited by batch processing, long reaction times, and scalability challenges. These factors complicate large-scale industrial production, as hydrothermal processes typically require sealed autoclaves and extended reaction times to achieve the desired crystallization and morphology control [8, 9].

### 3.2.3 Solid-state synthesis

Solid-state synthesis remains the most industrially adopted route due to simplicity, low cost, and scalability. This method involves high-temperature calcination (≥ 800–900 °C) of precursors such as $Li_2CO_3$ and $TiO_2$, where formation of spinel $Li_4Ti_5O_{12}$ proceeds through diffusion-controlled solid-state reactions and intermediate titanate phases, as elucidated by Shen et al. [10]. While it ensures reproducible phase formation, prolonged thermal treatment typically produces micrometer-sized particles with limited

microstructural control due to grain growth and agglomeration, as summarized in the LTO synthesis literature by Sun et al. [11]. Such coarse morphologies increase lithium diffusion length and charge-transfer resistance, which are unfavorable under aqueous conditions where interfacial kinetics dominate performance [11]. Σχήμα παρακαλώ με τα σχετικά SEM

## 3.3 Synthesis Comparison

The comparison of synthesis approaches highlights a fundamental trade-off between microstructural control and industrial scalability. For aqueous lithium-ion systems, where interfacial reactions and ion transport strongly determine electrochemical stability, nanoscale control becomes particularly important. Consequently, synthesis strategies capable of producing homogeneous, phase-pure, and nanosized $Li_4Ti_5O_{12}$ particles are expected to provide superior electrochemical behavior compared with coarse-grained materials [5 - 7, 11].

| **Synthesis Method** | **Typical Calcination temperature (°C)** | **Morphology & Particle size** | **Phase Purity** | **Advantages for Electrochemical Systems** | **Main limitations** | **Ref.** |
|---|---|---|---|---|---|---|
| Sol–gel | 600–700 | 50–200 nm nanoparticles | Excellent | Short diffusion length, high interface area, improved rate capability | Medium scalability | [5 - 7] |
| Hydrothermal | ≤500 + mild calcination | 20–100 nm tailored nanostructures | Excellent | High crystallinity, controlled morphology | Batch processing | [8, 9] |
| Solid-state | 800–900 | 0.5–5 μm particles | Good–Excellent | Industrial scalability | Long diffusion paths | [10, 11] |

***Table 3.1111:*** *Comparison of major $Li_4Ti_5O_{12}$ synthesis routes and their implications for electrochemical applications.*

The comparison presented in Table 3.1 indicates that, although solid-state synthesis remains industrially attractive, wet-chemical approaches provide decisive advantages. In particular, sol–gel synthesis offers an optimal balance between structural homogeneity, nanoscale particle control, and relatively moderate processing complexity [5 - 7]. Its ability to produce phase-pure $Li_4Ti_5O_{12}$ with reduced particle size directly addresses the kinetic and interfacial limitations identified in Chapters 1 and 2, where aqueous battery performance is governed primarily by electrolyte–electrode interactions rather than bulk structural degradation. The enhanced surface accessibility and shortened lithium diffusion pathways achievable through sol–gel synthesis are therefore expected to improve electrochemical utilization and stability under aqueous operating conditions [5 - 7, 11].

## 3.4 References


[1] T. Ohzuku, A. Ueda, and N. Yamamoto, “Zero-Strain Insertion Material of Li [ Li1 / 3Ti5 / 3 ] O 4 for Rechargeable Lithium Cells,” J. Electrochem. Soc., vol. 142, no. 5, pp. 1431–1435, May 1995, doi: 10.1149/1.2048592.

[2] T.-F. Yi, S.-Y. Yang, and Y. Xie, “Recent advances of $Li_4$ $Ti_5$ $O_{12}$ as a promising next generation anode material for high power lithium-ion batteries,” J. Mater. Chem. A, vol. 3, no. 11, pp. 5750–5777, 2015, doi: 10.1039/C4TA06882C.

[3] C. Julien, A. Mauger, K. Zaghib, and H. Groult, “Comparative Issues of Cathode Materials for Li-Ion Batteries,” Inorganics, vol. 2, no. 1, pp. 132–154, Mar. 2014, doi: 10.3390/inorganics2010132.

[4] X. Chen and S. S. Mao, “Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications,” Chem. Rev., vol. 107, no. 7, pp. 2891–2959, Jul. 2007, doi: 10.1021/cr0500535.

[5] J. Wang, X.-M. Liu, H. Yang, and X. Shen, “Characterization and electrochemical properties of carbon-coated Li4Ti5O12 prepared by a citric acid sol–gel method,” J. Alloys Compd., vol. 509, no. 3, pp. 712–718, Jan. 2011, doi: 10.1016/j.jallcom.2010.07.215.

[6] C. Zhang, Y. Zhang, J. Wang, D. Wang, D. He, and Y. Xia, “Li4Ti5O12 prepared by a modified citric acid sol–gel method for lithium-ion battery,” J. Power Sources, vol. 236, pp. 118–125, Aug. 2013, doi: 10.1016/j.jpowsour.2013.01.135.

[7] L. Zhang et al., “Electrochemical performance of Li4Ti5O12 anode material synthesised using polyethylene glycol as a template agent,” Ceram. Int., vol. 47, no. 4, pp. 4729–4736, Feb. 2021, doi: 10.1016/j.ceramint.2020.10.042.
[8] H.-Y. Wu, M.-H. Hon, C.-Y. Kuan, and I.-C. Leu, “Hydrothermal synthesis of $Li_4Ti_5O_{12}$ nanosheets as anode materials for lithium ion batteries,” RSC Adv., vol. 5, no. 44, pp. 35224–35229, 2015, doi: 10.1039/C5RA01351H.
[9] Y.-M. Jiang, K.-X. Wang, H.-J. Zhang, J.-F. Wang, and J.-S. Chen, “Hierarchical Li4Ti5O12/TiO2 composite tubes with regular structural imperfection for lithium ion storage,” Sci. Rep., vol. 3, no. 1, p. 3490, Dec. 2013, doi: 10.1038/srep03490.
[10] Y. Shen, M. Søndergaard, M. Christensen, S. Birgisson, and B. B. Iversen, “Solid State Formation Mechanism of $Li_4Ti_5O_{12}$ from an Anatase $TiO_2$ Source,” Chem. Mater., vol. 26, no. 12, pp. 3679–3686, Jun. 2014, doi: 10.1021/cm500934z.
[11] X. Sun, P. V. Radovanovic, and B. Cui, “Advances in spinel $Li_4Ti_5O_{12}$ anode materials for lithium-ion batteries,” New J. Chem., vol. 39, no. 1, pp. 38–63, 2015, doi: 10.1039/C4NJ01390E.

# 4. Fabrication and Immobilization of LTO Electrode

## 4.1 Importance of Uniformity and Adhesion

In ALIB systems, the immobilization of $Li_4Ti_5O_{12}$ onto the current collector represents a critical transition from intrinsic material properties to practical electrode performance. Although LTO benefits from a zero-strain lithiation mechanism and a relatively high working potential that thermodynamically suppresses hydrogen evolution, these advantages can be significantly compromised by poor electrode architecture. Uniform distribution of the active material and intimate contact with the current collector are therefore essential requirements for achieving reproducible electrochemical behavior, minimizing polarization losses, and ensuring long-term stability.

Non-uniform electrode coatings lead to spatially heterogeneous current-density distributions, where localized regions experience disproportionately high current loads. Several studies have demonstrated that such current-density hotspots promote localized overpotentials and uneven utilization of the active material due to nonuniform ionic and electronic transport pathways across the electrode thickness [1]. These effects become

particularly critical in aqueous systems where the narrow electrochemical stability window of water amplifies the impact of local polarization phenomena.

Electrode thickness further complicates this balance. While increasing thickness is often pursued to enhance areal capacity, thicker coatings inherently introduce longer ionic diffusion paths and higher electronic resistance. Beyond a critical thickness, diffusion limitations dominate the electrochemical response, leading to pronounced deterioration in rate capability unless tortuosity is reduced and continuous ionic and electronic pathways are preserved throughout the electrode depth [1]. Consequently, thickness optimization must be co-considered with porosity, microstructural uniformity, and conductive-network connectivity to avoid underutilization of the active material due to polarization losses.

Mechanical robustness and electrochemical continuity also depend strongly on adhesion between the electrode layer and the current collector. Insufficient adhesion may result in partial delamination during drying, electrolyte wetting, or prolonged cycling, disrupting electronic percolation and introducing irreversible interfacial resistance. Importantly, electrode drying is an active processing step: binder migration and compositional gradients induced by solvent evaporation have been identified as major contributors to coating detachment and mechanical stress development at the collector interface [2].

Binder chemistry therefore plays a decisive role in governing both adhesion and mechanical cohesion. Waterborne polymeric binders such as carboxymethyl cellulose (CMC) and styrene–butadiene rubber (SBR) are widely employed due to their environmental compatibility and favorable mechanical properties. Studies by Chang et al. and later binder-design reviews have shown that the CMC/SBR binder system forms an elastic three-dimensional polymer network that improves adhesion between the electrode coating and the current collector while maintaining electronic connectivity between active particles [3, 4]. Nevertheless, literature reports also indicate that these binders may exhibit swelling, dispersion instability, or non-uniform distribution if slurry formulation and drying conditions are not carefully controlled [2, 4].

Consequently, uniformity and adhesion should be considered intrinsically coupled design parameters rather than independent variables. Effective electrode fabrication strategies must therefore focus on the simultaneous optimization of coating thickness, particle distribution, and binder-mediated adhesion to minimize local overpotentials and ensure stable operation of aqueous LTO electrodes.

Within this context, the selection of an appropriate electrode fabrication technique becomes a critical step for translating the intrinsic properties of $Li_4Ti_5O_{12}$ into practical electrochemical performance. Among the available coating techniques, tape casting (doctor-blade coating) represents the most widely used industrial approach due to its simplicity, scalability, and compatibility with high-viscosity electrode slurries. However, several studies have shown that tape casting may lead to compositional

gradients, particle sedimentation, and binder migration during drying, particularly in water-based formulations [2].

Spray deposition has recently emerged as an alternative electrode fabrication strategy capable of producing highly uniform thin films through droplet-based deposition mechanisms. Because atomized droplets evaporate rapidly upon impact, sedimentation and phase separation effects can be significantly reduced, potentially leading to improved microstructural homogeneity and coating reproducibility [6,7]. Although spray coating has been widely explored for various lithium-ion battery materials, its application to $Li_4Ti_5O_{12}$ electrodes—particularly for aqueous lithium-ion battery systems—remains comparatively limited in the literature. This makes spray deposition an interesting processing route to investigate, as it may provide improved control over coating thickness, particle distribution, and adhesion for aqueous LTO electrodes. The following section therefore examines the spray deposition technique and its governing parameters before comparing it with the more conventional tape-casting approach.

## 4.2 Spray Deposition Technique

In spray deposition, the electrode slurry is atomized into fine droplets and transported toward the current collector substrate, where successive droplet impact and rapid solvent evaporation lead to gradual film formation. Compared with conventional tape casting, which forms a continuous wet film in a single step, spray deposition builds the electrode through the accumulation of multiple micro-layers. This droplet-based deposition mechanism enables improved control over coating thickness, particle distribution, and surface morphology, often resulting in more homogeneous coatings with reduced agglomeration of active particles [6, 7].

Spray deposition also offers practical advantages for aqueous electrode fabrication. The technique is particularly suitable for low-viscosity water-based slurries and facilitates rapid solvent evaporation due to the high surface-area-to-volume ratio of atomized droplets. These characteristics can enhance wetting of the current collector and reduce drying-induced mechanical stress within the electrode coating. As a result, spray deposition has been widely explored as a versatile electrode manufacturing approach capable of producing uniform coatings while maintaining good adhesion and microstructural control [6, 7].

However, the process introduces additional parameters that must be carefully optimized. Factors such as nozzle geometry, atomization pressure, spray distance, substrate temperature, and solvent evaporation rate strongly influence droplet spreading, coating uniformity, and the final electrode microstructure. Improper parameter selection may lead to excessive porosity, incomplete particle connectivity, or thickness nonuniformities, which can negatively affect electronic transport and electrochemical performance [6].

### 4.2.1 Principle of Spray Deposition

In spray deposition, a particle dispersion is atomized through a nozzle using compressed gas or ultrasonic excitation, generating micron-scale droplets that are directed toward the current collector substrate. Upon impact, the droplets spread across the surface, partially coalesce with neighboring droplets, and dry rapidly, forming thin layers that progressively accumulate into the final electrode coating. The resulting film formation process is therefore governed by repeated cycles of droplet deposition and solvent evaporation [6].

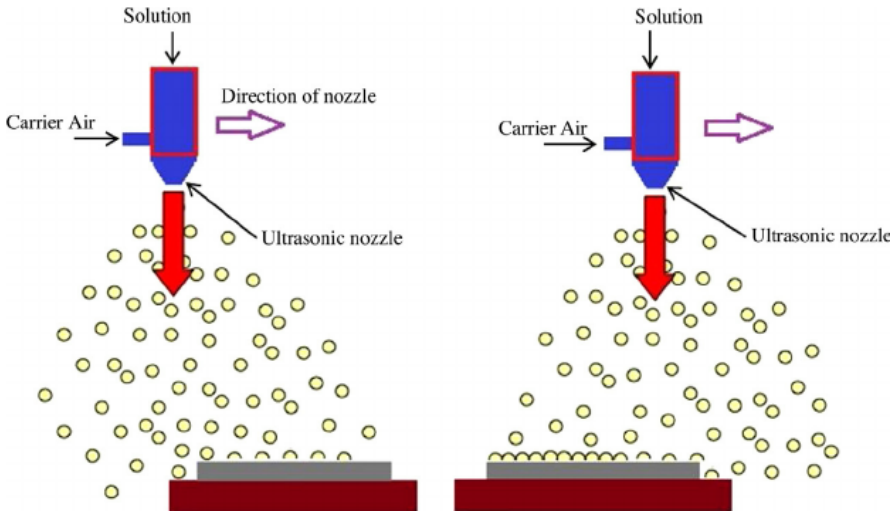



**Figure 4.1111:** Schematic diagram of the spray coating process, shown at two different times of a spray pass. Adopted from Lee et al. [6]

The coating morphology depends not only on the composition of the slurry—such as particle concentration, binder content, and viscosity—but also on process parameters including droplet size distribution, atomization pressure, substrate temperature, and evaporation kinetics. As shown in Figure 4.1, spray deposition relies on the atomization of the precursor dispersion into fine droplets that are transported toward the substrate. Rapid solvent evaporation during droplet flight and impact enables thin layers to form progressively, allowing improved control of film morphology compared with continuous coating methods. These parameters collectively control droplet spreading behavior, film formation dynamics, and the structural uniformity of the electrode layer.

### 4.2.2 Microstructural Uniformity

Microstructural uniformity represents a critical requirement for achieving reproducible electrochemical performance in lithium-ion battery electrodes. Non-uniform distribution of the active material, conductive additives, or binder can lead to spatial variations in ionic and electronic transport pathways, producing localized current-density gradients and uneven utilization of the electrode material.

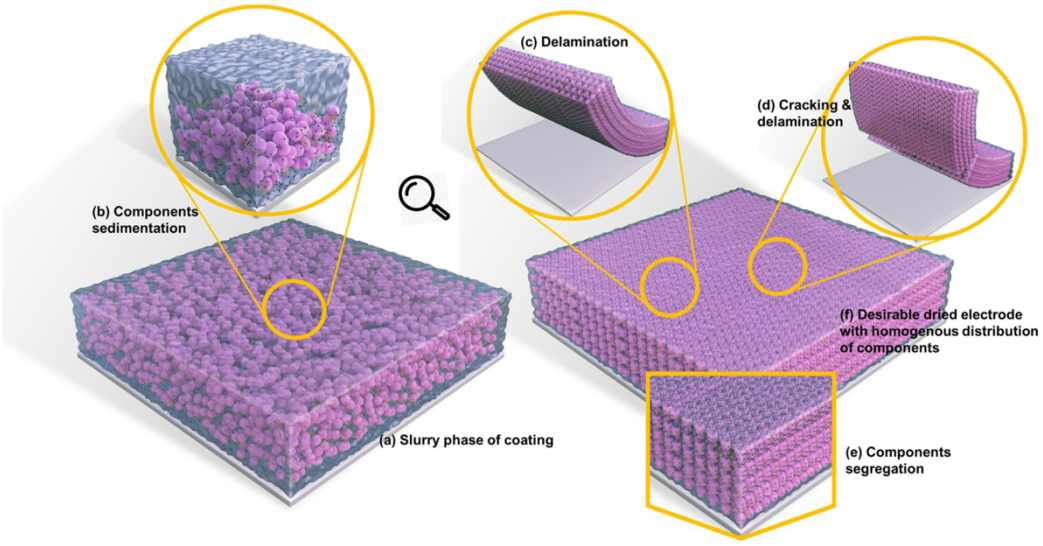



***Figure 4.2222:*** Schematic diagrams of the electrodes with coating defects. (a) Slurry phase of coating; (b) components sedimentation; (c) delamination of coating from current collector; (d) coating cracking and delamination; (e) components segregation; (f) desirable dried electrode coating with homogenous distribution of components. Adapted from Zhang et al. [4]

As illustrated in Figure 4.2, coating defects such as sedimentation, binder segregation, and interfacial delamination can lead to heterogeneous electrode structures that significantly affect electrochemical transport pathways and long-term cycling stability.

Spray deposition has emerged as an effective approach for improving coating homogeneity, particularly in aqueous electrode processing. In contrast to tape casting, where gravity-driven particle settling and solvent flow may induce phase separation during drying, spray deposition minimizes sedimentation effects due to the small droplet volume and the short residence time prior to solvent evaporation. As a result, the deposition process promotes a more homogeneous distribution of active material and conductive networks across the electrode thickness.

Manufacturing studies of lithium-ion battery electrodes have shown that coating processes strongly influence electrode microstructure and therefore electrochemical performance. For example, Park et al. [8] discussed advanced electrode fabrication routes—including spray- and dry-coating approaches—emphasizing that uniform distribution of active materials and binders is essential for achieving stable electrode architectures during battery manufacturing. More generally, analyses of electrode production processes highlight that coating uniformity and component dispersion directly affect ionic and electronic transport pathways within the electrode microstructure [9]. Consequently, droplet-based deposition techniques can mitigate transport inhomogeneities that are often amplified in aqueous electrode systems.

### 4.2.3 Thickness Control

Thickness control represents an additional advantage of spray deposition. The final coating thickness can be precisely tuned by adjusting process parameters such as spray rate, deposition time, nozzle–substrate distance, and the number of spray passes, while maintaining constant slurry composition.

Investigations of electrode architecture and degradation mechanisms indicate that the thickness and internal structure of battery electrodes significantly influence electrochemical performance and stability. For instance, Held et al. [10] demonstrated that electrode thickness strongly affects lithium-ion transport pathways and degradation behavior during cycling. In typical lithium-ion battery electrodes, coating thicknesses generally range between 30 and 120 μm, depending on the intended application and energy–power balance of the device. Electrodes thicker than approximately 100 μm frequently exhibit increased ionic transport resistance and non-uniform lithiation across the electrode thickness, which may accelerate degradation and reduce accessible capacity [10].

For $Li_4Ti_5O_{12}$ electrodes operating in aqueous electrolytes, this capability is particularly important. Because aqueous systems typically operate at lower voltages and rely heavily on fast ion transport, excessive electrode thickness can significantly amplify diffusion limitations. When electrode thickness exceeds roughly 80–100 μm, lithium ions must travel longer diffusion distances through the porous electrode structure, increasing polarization losses and reducing rate capability.

Conversely, very thin electrodes—typically below 20–30 μm—may provide excellent ionic transport and low polarization but often exhibit insufficient areal capacity due to the limited mass loading of active material. As a result, the energy-storage capability of the electrode becomes constrained despite favorable transport kinetics.

Spray deposition allows precise control over electrode thickness by gradually building the coating through multiple deposition passes. This layer-by-layer deposition strategy enables the fabrication of electrodes with controlled thickness typically in the 40–80 μm range, which represents a practical compromise between ionic transport accessibility and adequate areal capacity for battery operation.

Therefore, achieving controlled intermediate thicknesses through spray deposition provides an effective strategy for optimizing the balance between electrochemical accessibility, transport kinetics, and energy-storage performance in $Li_4Ti_5O_{12}$ electrodes for aqueous lithium-ion battery systems.

### 4.2.4 Drying Dynamics and Adhesion

Drying behavior constitutes one of the most significant distinctions between spray deposition and casting-based techniques. In spray deposition, solvent evaporation occurs rapidly due to the high surface-area-to-volume ratio of atomized droplets and the presence of convective airflow. The evaporation rate is governed by droplet size, solvent volatility, substrate temperature, and ambient gas flow.

Experimental and modeling studies on LIB electrode manufacturing have shown that drying conditions strongly influence component redistribution within the porous electrode, especially binder and conductive additive migration, which can directly impact adhesion to the current collector and internal resistance. In particular, rapid solvent removal can alter the consolidation pathway of particulate films and promote through-thickness gradients, while temperature-driven drying-rate changes have been linked to measurable shifts in binder distribution and adhesion strength [11 - 13]. As discussed in Section 4.1, binder distribution is a decisive factor for mechanical cohesion and interfacial stability in aqueous processing; therefore, controlling drying kinetics in spray-deposited electrodes is critical to minimize binder segregation, prevent interfacial weakening, and reduce the risk of delamination during cycling [11, 14]

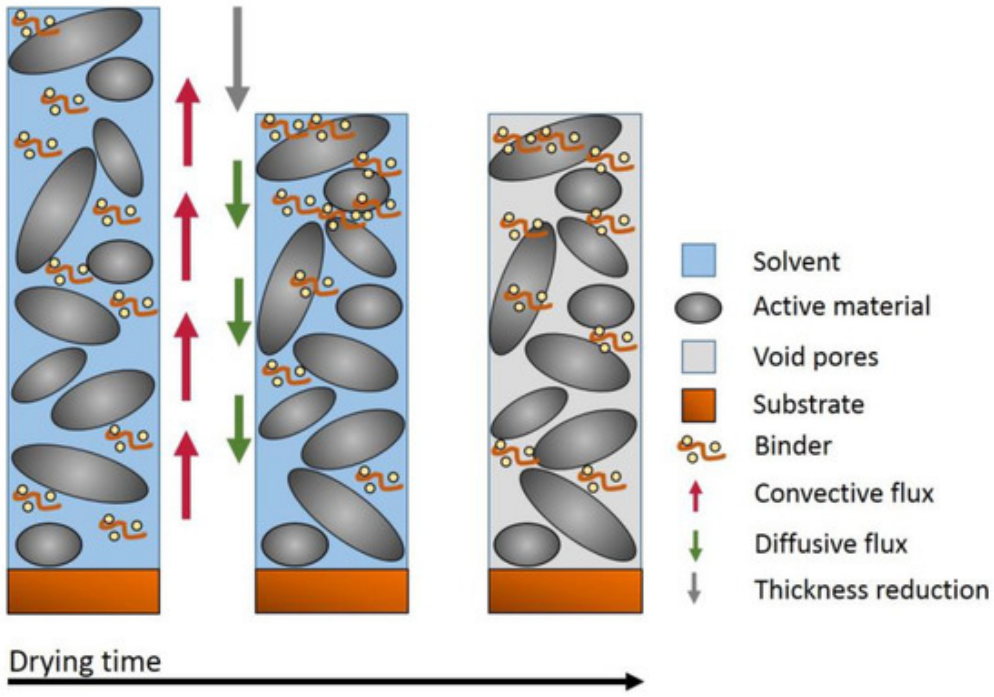



***Figure 4.3333:*** Schematic illustration of binder migration during the drying of lithium-ion battery electrodes. Solvent evaporation induces convective flow within the coating layer, which can transport binder toward the surface and generate concentration gradients across the electrode thickness. Adapted from Zihrul et al., Batteries [14]).

As illustrated in Figure 4.3, solvent evaporation during electrode drying can induce binder migration toward the coating surface, generating compositional gradients across the electrode thickness and influencing adhesion and mechanical stability of the electrode layer [14].

### 4.2.5 Process Parameters and Polyparametric Nature

Despite its advantages, spray deposition is intrinsically polyparametric and highly sensitive to processing conditions. The morphology, thickness uniformity, and adhesion of the deposited electrode layer are governed by several interdependent parameters, including nozzle–substrate distance, spray rate, substrate temperature, atomization pressure, and solids concentration of the dispersion.

Literature studies on spray-processed battery electrodes indicate that the nozzle–substrate distance typically ranges between approximately 10 and 20 cm, allowing

atomized droplets to partially evaporate before reaching the substrate while maintaining sufficient kinetic energy for uniform spreading [7]. Shorter distances may promote droplet coalescence and non-uniform wetting, whereas excessively large distances can lead to premature solvent evaporation and powder-like or discontinuous coatings [7, 11].

Substrate temperature represents another key parameter controlling solvent evaporation and film consolidation. Many experimental spray-coating studies report substrate temperatures in the range of roughly 60–120 °C, where solvent evaporation is sufficiently rapid to prevent droplet accumulation while avoiding excessive thermal stresses that could degrade coating adhesion or induce cracking [7, 11]. For example, spray-deposited battery electrodes are commonly dried near ~100 °C to remove solvent residues and stabilize the electrode film structure [7, 11].

The spray flow rate is typically maintained in the order of ~0.5–2 mL $min^{-1}$, depending on slurry viscosity and solids loading. Higher flow rates increase deposition speed but can produce thicker wet films and droplet coalescence, whereas excessively low flow rates may lead to discontinuous coatings with poor electronic connectivity. In addition, atomization pressures typically between about 0.5 and 2 bar are frequently used to generate droplets with diameters in the tens-of-micrometers range, enabling uniform surface coverage [8].

More generally, electrode manufacturing studies have demonstrated that process parameters strongly influence the resulting electrode microstructure and therefore the electrochemical performance of lithium-ion batteries, highlighting the critical importance of carefully controlling deposition and drying conditions during electrode fabrication [8, 9, 13]

These observations highlight that spray deposition shifts the complexity of electrode fabrication from bulk film formation to droplet-scale deposition and drying control, where the interplay between droplet evaporation, spreading, and consolidation ultimately determines the final electrode microstructure and electrochemical performance.

### 4.2.6 Dispersion versus Slurry Considerations in Aqueous Spray Processing

In aqueous spray deposition, the formulation must be considered primarily as a particle dispersion rather than a conventional slurry. Unlike slurries used in tape casting—which rely on yield stress and shear-thinning behavior to maintain film integrity—spray deposition requires highly stable dispersions with well-controlled particle–particle interactions to prevent agglomeration and nozzle clogging during atomization.

A key factor governing dispersion stability is the balance between electrostatic repulsion and attractive van der Waals interactions between particles. In aqueous electrode formulations, this balance is commonly controlled through pH adjustment and the use of dispersants or polymeric binders, which modify surface charge and steric interactions between particles. For example, carboxymethyl cellulose (CMC), widely used in aqueous lithium-ion battery electrodes, introduces negatively charged

carboxylate groups that increase electrostatic repulsion between particles and improve dispersion stability [3, 4]. Direct observations of graphite electrodes prepared with CMC/SBR binders have shown that appropriate binder distribution can significantly improve particle dispersion and electrode homogeneity [3].

The pH of the dispersion also plays a decisive role in determining colloidal stability. Adjusting pH modifies the surface charge of oxide particles and therefore the electrostatic double layer surrounding them. Studies of aqueous electrode processing have shown that maintaining pH values away from the particle isoelectric point enhances electrostatic stabilization and suppresses agglomeration during mixing and deposition [4]. In practical electrode formulations, mild alkaline conditions are frequently employed to promote stable dispersions and improve binder adsorption on particle surfaces.

Additional stabilization may be achieved through steric hindrance provided by polymeric additives, such as polyacrylic acid (PAA) or CMC, which form adsorbed layers on particle surfaces and reduce aggregation during dynamic processes such as spraying and drying. Experimental studies on electrode drying and film formation have demonstrated that the distribution and interaction of binders and conductive additives within aqueous dispersions strongly influence coating uniformity and mechanical integrity [12, 13].

Consequently, in spray-based aqueous electrode fabrication, formulation optimization must focus not only on viscosity and solids loading but also on dispersion stability under dynamic atomization conditions, where droplet formation, evaporation, and particle interactions occur simultaneously. Small variations in pH, binder concentration, or dispersant chemistry can therefore lead to substantial changes in droplet formation, coating morphology, and ultimately electrochemical performance.

### 4.2.7 Summary

Overall, the literature indicates that spray deposition represents a promising electrode fabrication approach capable of providing precise control over coating formation through deposition parameters rather than extensive slurry formulation adjustments. The droplet-based deposition mechanism can produce relatively uniform thin films while reducing sedimentation effects and limiting large-scale binder migration during drying. As a result, spray processing has been explored as a coating strategy for various lithium-ion battery materials, particularly in applications requiring controlled thin films or homogeneous electrode microstructures.

However, systematic investigations of spray-deposited $Li_4Ti_5O_{12}$ electrodes remain relatively limited compared with more established fabrication techniques. Most reported LTO electrodes have been produced using conventional slurry-based coating processes such as tape casting or doctor-blade coating, which remain the dominant manufacturing methods in lithium-ion battery technology. Consequently, the potential advantages of spray deposition for aqueous LTO electrodes—such as improved coating uniformity, controllable thickness, and reduced drying-induced segregation—have not yet been extensively explored in the literature.

The preceding sections have shown that the performance of spray-processed electrodes depends strongly on the optimization of dispersion stability, atomization conditions, and drying dynamics, which collectively determine the final electrode microstructure and the continuity of ionic and electronic transport pathways. In order to place these considerations into context, the following section examines tape casting (doctor-blade coating)—the most widely used electrode fabrication technique—and discusses its coating formation mechanisms and practical characteristics as a basis for comparison with spray deposition. Therefore, understanding the differences between droplet-based deposition and conventional slurry casting is essential for evaluating their suitability for aqueous LTO electrode fabrication.

## 4.3 Tape Casting (Doctor-Blade) Technique

Tape casting, often implemented through the doctor-blade approach, is among the most established and industrially mature techniques for electrode fabrication. While the two terms are frequently used interchangeably in the battery literature, doctor blading typically refers to laboratory-scale, batch deposition using a fixed blade, whereas tape casting denotes a continuous process compatible with industrial roll-to-roll manufacturing. In both cases, a continuous wet film is deposited onto the current collector, with the final coating thickness primarily governed by the blade gap and the rheological properties of the slurry.

From a processing perspective, tape casting is inherently compatible with aqueous formulations, provided that slurry viscosity, dispersion stability, and drying conditions are carefully controlled. Numerous studies have reported the successful fabrication of homogeneous LTO composite electrodes using water-based systems comprising active material, conductive carbon, and polymeric binders such as CMC or SBR [3, 4]. Compared with organic-solvent-based routes, aqueous tape casting offers clear environmental and safety advantages; however, it also introduces increased sensitivity to drying-induced stresses and binder redistribution phenomena that must be carefully managed to preserve coating uniformity and adhesion.

The principal advantage of tape casting lies in its ability to produce thick, mechanically robust electrodes with high mass loading. Typical dry-film thicknesses obtained through doctor-blade coating range from approximately 30–150 μm, while industrial tape-cast electrodes can reach 200 μm or more, corresponding to mass loadings in the range of 5–20 mg $cm^{-2}$ depending on formulation and application [7, 8]. This capability is particularly attractive for stationery and grid-scale energy storage systems, where areal and volumetric energy density are prioritized over gravimetric metrics. For LTO, which exhibits excellent cycling stability but moderate theoretical capacity, increased mass loading is often pursued to compensate for intrinsic capacity limitations. Tape casting therefore provides a practical pathway toward industrially relevant electrode architectures that are difficult to realize using spray-based techniques.

Nevertheless, increasing electrode thickness introduces pronounced transport limitations unless specific architectural strategies are implemented. Thick tape-cast LTO electrodes frequently exhibit gradients in porosity, binder concentration, and conductive additive distribution as a result of non-uniform solvent evaporation during drying [2,11]. These gradients increase ionic tortuosity and electronic resistance,

leading to elevated polarization and reduced rate capability. Such effects become particularly critical in aqueous electrolytes, where diffusion constraints and interfacial kinetics are already more restrictive than in non-aqueous systems [1].

Figure 4.4 illustrates the physical processes occurring during electrode drying. Solvent evaporation from the coating surface induces convective flow within the wet electrode layer, redistributing binder and conductive additives during film solidification. This process ultimately determines the final microstructure of the electrode, including particle packing and binder distribution within the porous structure [15].

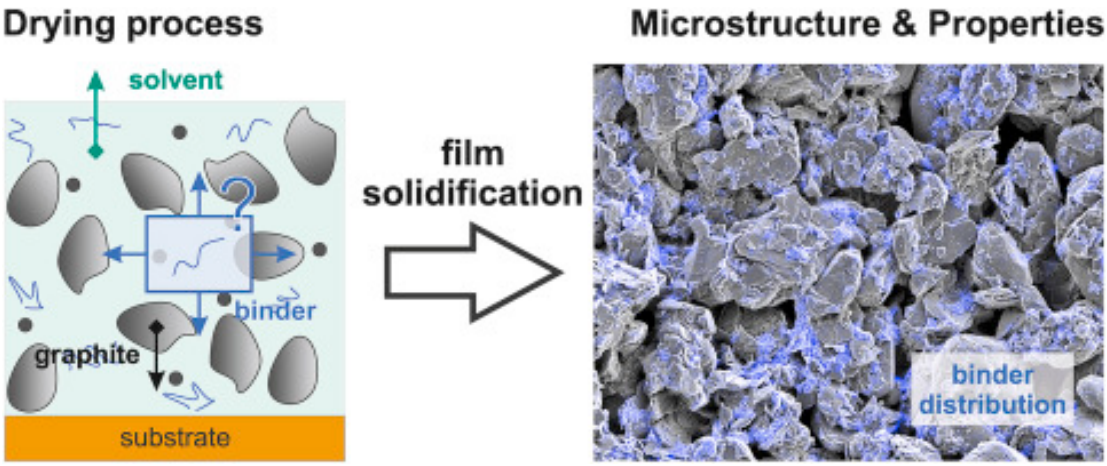



***Figure 4.4444:*** Schematic representation of the drying process in lithium-ion battery electrodes and the resulting electrode microstructure after film solidification. Solvent evaporation from the coating surface induces convective transport within the slurry layer, redistributing binder and conductive additives and influencing the final electrode microstructure. Adapted from Jaiser et al. [15].

Experimental evidence of binder redistribution during electrode drying is presented in Figure 4.5. As the drying rate increases, the binder tends to migrate toward the electrode surface, leading to enrichment near the drying front and depletion close to the current collector interface. Such through-thickness compositional gradients may weaken adhesion at the electrode–collector interface and increase internal resistance, potentially leading to delamination and reduced electrochemical performance during cycling [15].

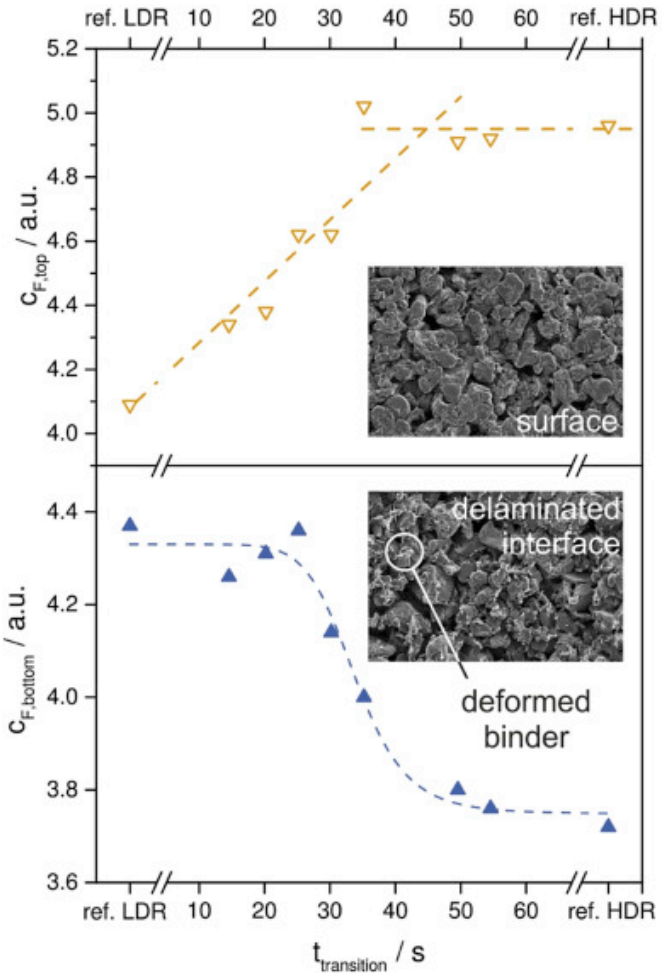



***Figure 4.5555:*** Experimental analysis of binder distribution in lithium-ion battery electrodes under different drying conditions. Increasing drying rates promote binder accumulation near the electrode surface and depletion near the current collector interface, leading to structural gradients that can affect adhesion and transport properties. Adapted from Jaiser et al. [15].

Binder selection and rheological optimization therefore play a central role in controlling slurry stability and coating formation in tape casting. Unlike spray deposition, where atomization imposes strict requirements on dispersion stability, tape casting relies primarily on controlled slurry rheology, typically exhibiting shear-thinning behavior that enables uniform spreading beneath the blade while maintaining film integrity after deposition. Comparative studies have shown that CMC-based aqueous binder systems provide strong adhesion and mechanical cohesion, but excessive binder content can block pore networks and hinder electrolyte infiltration [3, 4]. Conversely, insufficient binder leads to brittle coatings prone to cracking and delamination. The presence of conductive carbon further complicates formulation control by simultaneously enhancing electronic percolation and altering slurry viscosity and drying behavior.

A key distinction between tape casting and spray deposition lies in their drying dynamics. In tape-cast films, solvent evaporation predominantly occurs at the exposed film surface, generating concentration gradients that drive binder and fine-particle migration toward the drying front. Both experimental observations and modelling studies have identified this mechanism as a major contributor to interfacial adhesion loss and partial delamination in thick aqueous electrodes [2,5,11]. Although staged drying and controlled evaporation strategies can mitigate these effects, they introduce additional process complexity and extended manufacturing times.

Despite these limitations, tape casting remains a cornerstone of industrial electrode manufacturing due to its scalability, reproducibility, and compatibility with continuous roll-to-roll processing [8,9]. Recent studies suggest that advanced architectural strategies—such as porosity grading, multilayer electrode structures, or structured current collectors—can partially overcome transport limitations while retaining high mass loading [9,13].

In summary, tape casting remains particularly well suited for applications requiring thick, mechanically stable coatings and industrial scalability. A more direct comparison between tape casting and spray deposition is presented in the following section.

## 4.4 Comparative Evaluation of Spray Deposition and Tape Casting

Schematic representations are particularly useful for visualizing the fundamental differences between electrode fabrication techniques, as they directly illustrate how deposition pathways influence film formation, thickness control, and microstructural evolution. In the context of aqueous LTO-based anodes, Figure 4.6 highlights the contrasting principles of spray deposition and tape casting, which underline the distinct performance trends discussed throughout this chapter.

In spray deposition (Figure 4.6a), the electrode is formed through successive deposition of atomized droplets that rapidly dry upon contact with the substrate. This incremental layer-by-layer growth minimizes particle sedimentation and limits binder and conductive additive migration during solvent evaporation. As a result, spray-coated electrodes typically exhibit high lateral uniformity and relatively homogeneous through-thickness composition. In contrast, tape casting (Figure 4.6b) involves the deposition of a continuous wet film with predefined thickness, where solvent evaporation occurs predominantly from the exposed film surface. As demonstrated by Font et al. [2] and further analyzed by Jaiser et al. [11], this drying mechanism can generate concentration gradients within thick coatings, promoting binder and additive migration toward the evaporation front unless drying conditions are carefully controlled.

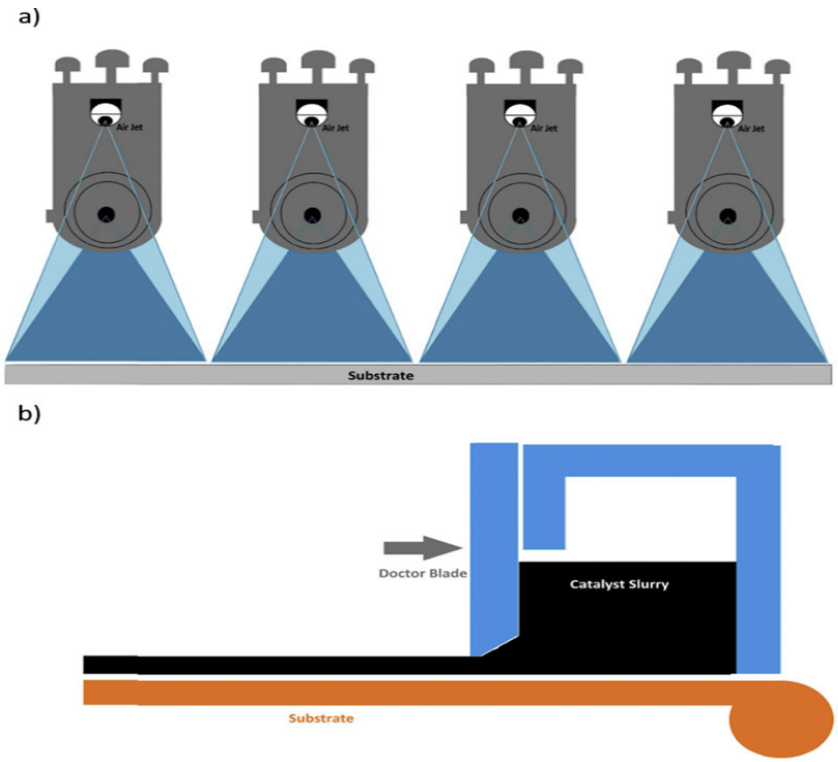



***Figure 4.6666:*** *Schematic illustration of electrode fabrication methods showing (a) spray coating and (b) tape casting processes. Adopted from Font et al. [2]*

Building upon this mechanistic framework, several studies have examined how these fabrication approaches influence electrode microstructure and electrochemical behavior. Lee and Grant [6] reported that spray fabrication can produce highly uniform electrode layers due to the droplet-based deposition mechanism, which limits large-scale particle sedimentation during coating formation. Similarly, Aivaliotis and Vernardou [7] demonstrated that spray-deposited electrodes exhibit improved lateral uniformity and reproducibility compared with conventional slurry casting approaches. Comparable observations were reported by Held et al. [10], who attributed the enhanced electrochemical stability of spray-coated electrodes to the reduced formation of drying-induced microstructural gradients.

Nevertheless, spray deposition does not universally outperform tape casting. While spray-coated electrodes often display superior microstructural uniformity at thin-to-moderate thicknesses, multilayer buildup at higher loadings may introduce transport limitations unless porosity and layer architecture are carefully controlled. Modeling work by Liu et al. [13] indicates that electrode performance becomes increasingly sensitive to transport pathways as thickness increases, emphasizing the need for optimized architecture in multilayer spray coatings.

Tape casting, by contrast, remains the most established technique for producing thick, high-loading electrodes compatible with industrial roll-to-roll manufacturing. Reviews by Arslan et al. [9] and Park et al. [8] highlight tape casting as a cornerstone technology in modern lithium-ion battery manufacturing due to its scalability and process reproducibility. This capability is particularly important for stationery and grid-scale energy storage applications, where areal capacity and mechanical robustness are prioritized. However, as demonstrated experimentally by Font et al. [2] and Jaiser et al.

[11], thick tape-cast electrodes frequently develop through-thickness gradients in porosity, binder concentration, and conductive additive distribution due to non-uniform solvent evaporation during drying. These gradients increase ionic tortuosity and electronic resistance, which can lead to elevated polarization during electrochemical cycling.

Consequently, spray deposition is particularly well suited for thin or moderately thick electrodes where uniformity and interfacial stability dominate performance. Tape casting, on the other hand, remains advantageous for thick, high-loading electrodes and scalable manufacturing environments. Rather than representing competing technologies, the two fabrication strategies should therefore be viewed as complementary approaches whose suitability depends strongly on the targeted electrode architecture and performance requirements, as emphasized in recent electrode manufacturing analyses [8, 9, 13].

To facilitate a systematic comparison beyond qualitative discussion, the key characteristics of spray deposition and tape casting reported in the literature are summarized in Table 4.1. Presenting these parameters side by side highlights the inherent trade-offs between uniformity, adhesion, transport, and scalability when each method is applied to LTO-based aqueous anodes.

| Criterion | Spray Deposition | Tape Casting | Ref. |
|---|---|---|---|
| **Typical thickness regime** | Thin to moderate coatings (≈5–80 μm); thickness controlled via spray rate, number of passes, and deposition time | Moderate to thick coatings (≈30–200 μm); thickness primarily controlled by blade gap and slurry solids loading | [6- 9] |
| **Coating uniformity** | High lateral uniformity due to incremental droplet deposition and minimal particle sedimentation | High uniformity achievable but sensitive to slurry rheology and drying-induced gradients | [6, 10, 11] |
| **Adhesion to current collector** | Generally strong when binder distribution is preserved through rapid droplet drying | Strong cohesion possible; risk of delamination increases with thickness and binder migration | [2, 3, 11] |
| **Sensitivity to drying dynamics** | Lower risk of severe binder migration due to fast droplet evaporation | High sensitivity: top-down drying may induce binder and additive segregation | [2, 11, 12] |
| **Formulation constraints** | Requires stable aqueous dispersions; sensitive to agglomeration and nozzle clogging | Requires precise control of slurry viscosity, binder/carbon balance, and dispersion stability | [3, 4] |
| **Scalability and manufacturing relevance** | Suitable for controlled coatings and research-scale uniformity studies; scalable with optimized spray systems | Highly compatible with roll-to-roll industrial processing and high-throughput manufacturing | [8, 9, 13] |

***Table 4.1111:*** *Comparative summary of spray deposition and tape casting techniques for LTO-based aqueous anodes, highlighting trade-offs in thickness control, uniformity, adhesion, formulation sensitivity, and scalability.*

As summarized in Table 4.1, spray deposition and tape casting occupy complementary positions within the electrode fabrication landscape. Spray deposition typically offers superior lateral uniformity and fine control over thin coatings due to its droplet-based deposition mechanism, which reduces sedimentation and suppresses large-scale binder migration during drying [6, 7, 10]. In contrast, tape casting enables higher mass loading and greater compatibility with industrial-scale manufacturing processes, particularly within continuous roll-to-roll electrode production lines [8, 9].

Importantly, neither technique is intrinsically superior across all fabrication criteria. Instead, the choice of electrode fabrication strategy must be aligned with the intended thickness regime, electrode architecture, and application-specific performance requirements. As demonstrated in studies of electrode drying and microstructural evolution, transport limitations and binder redistribution increasingly dominate electrode behavior as thickness increases, highlighting the importance of fabrication–structure coupling in determining electrochemical performance [2, 11, 13].

Overall, this comparative evaluation underscores a central theme of this thesis: the successful translation of LTO's favorable material-level properties into stable and reproducible aqueous battery performance depends on the coherent integration of synthesis, electrode architecture, and fabrication strategy. The synthesis–immobilization–architecture continuum therefore emerges as a fundamental design axis for the development of next-generation aqueous lithium-ion batteries.

## 4.5 References


[1] J. Newman and K. E. Thomas-Alyea, Electrochemical Systems, 3rd ed. Wiley, 2004.

[2] F. Font, B. Protas, G. Richardson, and J. M. Foster, "Binder migration during drying of lithium-ion battery electrodes: Modelling and comparison to experiment," J. Power Sources, vol. 393, pp. 177–185, Jul. 2018, doi: 10.1016/j.jpowsour.2018.04.097.

[3] W. J. Chang et al., "Direct Observation of Carboxymethyl Cellulose and Styrene–Butadiene Rubber Binder Distribution in Practical Graphite Anodes for Li-Ion Batteries," ACS Appl. Mater. Interfaces, vol. 11, no. 44, pp. 41330–41337, Nov. 2019, doi: 10.1021/acsami.9b13803.

[4] L. Zhang et al., "Exploring More Functions in Binders for Lithium Batteries," Electrochem. Energy Rev., vol. 6, no. 1, p. 36, Dec. 2023, doi: 10.1007/s41918-023-00198-2.

[5] D. L. Wood, J. Li, and C. Daniel, "Prospects for reducing the processing cost of lithium ion batteries," J. Power Sources, vol. 275, pp. 234–242, Feb. 2015, doi: 10.1016/j.jpowsour.2014.11.019.

[6] S. Ho Lee and P. S. Grant, "Spray fabrication of additive-free electrodes for advanced Lithium-Ion storage technologies," J. Colloid Interface Sci., vol. 651, pp. 742–749, Dec. 2023, doi: 10.1016/j.jcis.2023.07.211.

[7] D. Aivaliotis and D. Vernardou, "An Affordable Dual Purpose Spray Setup for Lithium-Ion Batteries Thin Film Electrode Deposition," Materials, vol. 17, no. 20, p. 5114, Oct. 2024, doi: 10.3390/ma17205114.

[8] J. Park, J. Kim, J. Kim, M. Kim, T. Song, and U. Paik, "Sustainable and cost-effective electrode manufacturing for advanced lithium batteries: the roll-to-roll dry coating process," Chem. Sci., vol. 16, no. 16, pp. 6598–6619, 2025, doi: 10.1039/D5SC00059A.

[9] K. Arslan, K. B. Dermenci, J. Van Mierlo, and M. Berecibar, "Current and future trends in lithium-ion battery electrode production machinery: A comprehensive review," Appl. Energy, vol. 402, p. 126968, Jan. 2026, doi: 10.1016/j.apenergy.2025.126968.

[10] T. Held, W. Hagemeier, D. Leykam, and C. Roth, "Understanding degradation mechanisms in spray-coated alternating silicon-carbon thin films as anodes for lithium-ion batteries," Electrochimica Acta, vol. 525, p. 146123, Jun. 2025, doi: 10.1016/j.electacta.2025.146123.

[11] S. Jaiser, M. Müller, M. Baunach, W. Bauer, P. Scharfer, and W. Schabel, "Investigation of film solidification and binder migration during drying of Li-Ion battery anodes," J. Power Sources, vol. 318, pp. 210–219, Jun. 2016, doi: 10.1016/j.jpowsour.2016.04.018.

[12] N. Kumano, Y. Yamaguchi, Y. Akimoto, A. Ohshima, H. Nakamura, and M. Yamamura, "Migration of binder and conductive agent during drying process of Li-ion battery cathodes," J. Power Sources, vol. 591, p. 233883, Jan. 2024, doi: 10.1016/j.jpowsour.2023.233883.

[13] C. Liu, T. Lombardo, J. Xu, A. C. Ngandjong, and A. A. Franco, "An experimentally-validated 3D electrochemical model revealing electrode manufacturing parameters' effects on battery performance," Energy Storage Mater., vol. 54, pp. 156–163, Jan. 2023, doi: 10.1016/j.ensm.2022.10.035.

[14] C. Zihrul, M. Lippke, and A. Kwade, “Model Development for Binder Migration within Lithium-Ion Battery Electrodes during the Drying Process,” Batteries, vol. 9, no. 9, p. 455, 2023. doi: 10.3390/batteries9090455.

[15] S. Jaiser, M. Müller, M. Baunach, W. Bauer and H. Nirschl, “Investigation of film solidification and binder migration during drying of Li-ion battery anodes,” Journal of Power Sources, vol. 318, pp. 210–219, 2016. doi: 10.1016/j.jpowsour.2016.04.018

# 5. Discussion – Overall Review

## 5.1 Summary of Key Findings

The literature reviewed throughout the previous chapters highlights the growing scientific interest in ALIBs as safe and environmentally benign alternatives to conventional non-aqueous lithium-ion systems. The primary motivation behind this research direction lies in the intrinsic safety, low cost, and non-flammability of aqueous electrolytes, which make them particularly attractive for stationary and large-scale energy-storage applications. However, the narrow thermodynamic stability window of water and the resulting parasitic reactions at electrode interfaces remain key limitations that must be addressed to achieve stable and efficient operation.

Within this context, $Li_4Ti_5O_{12}$ has emerged as one of the most promising anode materials for aqueous battery systems. The spinel structure of LTO enables a near zero-strain lithium insertion mechanism, which provides excellent structural stability during repeated lithiation and delithiation cycles. Moreover, the relatively high working potential of LTO compared with graphite reduces the thermodynamic driving force for hydrogen evolution, making it more compatible with aqueous electrolytes. As a result, LTO has become a widely investigated model anode material for studying electrode–electrolyte interactions in water-based battery systems.

The literature further demonstrates that the electrochemical performance of LTO is strongly influenced by synthesis conditions and resulting microstructural characteristics. Particle size, phase purity, crystallinity, and surface chemistry all play critical roles in determining lithium diffusion kinetics, electronic conductivity, and interfacial stability. Wet-chemical synthesis routes such as sol–gel and hydrothermal methods offer enhanced control over these parameters compared with conventional solid-state synthesis, enabling the production of nanoscale particles with improved electrochemical accessibility. However, these synthesis methods also introduce trade-offs between microstructural control, processing complexity, and scalability.

In addition to material synthesis, electrode fabrication and immobilization strategies represent a crucial step in translating intrinsic material properties into practical electrochemical performance. The literature reviewed in Chapter 4 clearly demonstrates that electrode architecture—including thickness, porosity, uniformity, and adhesion to the current collector—plays a decisive role in determining transport pathways and interfacial stability in aqueous systems. Even materials with favorable intrinsic properties may exhibit poor electrochemical performance if the electrode microstructure does not provide continuous ionic and electronic transport networks.

## 5.2 Critical Assessment of Electrode Fabrication Techniques

The comparative analysis of spray deposition and tape casting highlights the fundamental role of fabrication strategy in controlling electrode morphology and performance. Spray deposition produces electrode layers through incremental droplet deposition and rapid solvent evaporation. This mechanism inherently suppresses large-

scale particle sedimentation and reduces binder migration during drying, often resulting in highly uniform coatings with homogeneous composition across the electrode thickness. Such characteristics are particularly beneficial in aqueous systems, where localized current-density heterogeneities can accelerate parasitic reactions and reduce Coulombic efficiency.

However, spray deposition is not without limitations. The technique requires stable dispersions with carefully controlled particle–particle interactions, and the deposition process itself is highly sensitive to parameters such as spray rate, atomization pressure, substrate temperature, and nozzle–substrate distance. At higher loadings, multilayer buildup may introduce transport limitations unless electrode porosity and architecture are carefully engineered.

Tape casting, in contrast, remains the most widely used electrode fabrication method in industrial lithium-ion battery manufacturing. Its primary advantage lies in the ability to produce thick electrodes with high mass loading, which is essential for achieving high areal capacity in practical devices. Tape casting is also inherently compatible with continuous roll-to-roll manufacturing processes, making it highly attractive for large-scale production.

Nevertheless, the literature consistently indicates that thick tape-cast electrodes may develop concentration gradients in binder distribution, conductive additive content, and porosity during drying. These gradients increase ionic tortuosity and electronic resistance, which can lead to elevated polarization and reduced rate capability during electrochemical cycling. Such effects are particularly pronounced in aqueous electrolytes, where transport limitations and interfacial reactions already constrain electrochemical stability.

Taken together, these findings demonstrate that spray deposition and tape casting should not be viewed as competing techniques but rather as complementary fabrication strategies. Spray deposition offers superior control over coating uniformity and microstructural homogeneity in thin or moderately thick electrodes, whereas tape casting provides clear advantages in terms of scalability and high mass loading. The optimal fabrication method therefore depends strongly on the targeted electrode architecture and application requirements.

## 5.3 Interplay Between Material Properties, Electrolyte Chemistry, and Electrode Architecture

A central conclusion emerging from this work is that electrochemical performance in ALIBs cannot be attributed to a single material parameter. Instead, performance arises from the combined interaction between active material properties, electrolyte chemistry, and electrode architecture.

LTO provides excellent structural stability and a relatively favorable working potential for aqueous environments, yet these intrinsic advantages alone are insufficient to guarantee stable battery operation. The electrode must also provide efficient transport pathways for both lithium ions and electrons while maintaining mechanical integrity and stable interfaces with the electrolyte. At the same time, electrolyte composition

influences interfacial reactions, pH stability, and parasitic gas evolution processes that directly affect electrode stability.

Consequently, the design of high-performance aqueous lithium-ion batteries requires a holistic approach that simultaneously considers material synthesis, electrode fabrication, and electrolyte selection. Improvements in only one component of the system are unlikely to produce substantial performance gains if the remaining elements remain poorly optimized.

## 5.4 Identification of Research Gaps

Despite the significant progress achieved in recent years, several important challenges remain in the development of LTO-based aqueous battery systems. First, the relationship between electrode fabrication parameters and electrochemical performance remains insufficiently understood, particularly for spray-based deposition techniques. While numerous studies have demonstrated improved uniformity in spray-coated electrodes, systematic investigations linking process parameters to resulting electrode microstructure and transport properties remain limited. Second, most studies investigate either material synthesis or electrode fabrication independently, without considering the combined effects of these processes on final device performance. A more integrated approach that connects synthesis methods, particle morphology, electrode architecture, and electrolyte chemistry could provide valuable insight into performance optimization. Finally, the majority of experimental studies have focused on half-cell configurations rather than full aqueous battery systems. The development of stable aqueous full cells, including compatible cathode materials and optimized electrolyte formulations, remains a critical step toward practical implementation. These research gaps suggest that future work should increasingly focus on system-level optimization rather than isolated improvements in individual components. Such an approach will be essential for translating the favorable properties of LTO into practical aqueous energy-storage technologies.

# 6. Perspectives

## 6.1 Future Experimental Design

The analysis presented throughout this thesis highlights several opportunities for future experimental investigations aimed at improving the performance of ALIBs based on LTO anodes. While the literature provides extensive insight into individual aspects of material synthesis, electrode fabrication, and electrolyte design, fewer studies have systematically explored the combined influence of these parameters within a unified experimental framework.

Future experimental work could therefore focus on establishing a controlled experimental matrix in which synthesis method, electrode architecture, and electrolyte composition are varied simultaneously. Such an approach would enable a more

comprehensive understanding of how microstructural characteristics of LTO particles interact with electrode morphology and electrolyte chemistry to determine electrochemical performance. In particular, systematic variation of particle size, electrode thickness, and binder composition could provide valuable insight into the relationship between microstructure, transport pathways, and interfacial stability.

Another promising direction involves the detailed investigation of spray-deposited electrodes under controlled fabrication conditions. Although spray deposition has demonstrated advantages in terms of coating uniformity and reduced binder migration, its polyparametric nature means that small changes in process parameters can significantly influence electrode microstructure. Future experiments could therefore examine the effects of parameters such as spray rate, substrate temperature, and droplet size distribution on electrode porosity, adhesion, and electrochemical behavior. Such studies would help establish reproducible processing windows for spray-based fabrication of aqueous battery electrodes.

## 6.2 Exploration of Advanced Electrolyte Concepts

Electrolyte design remains one of the most critical factors limiting the performance of ALIBs. The narrow electrochemical stability window of water constrains the achievable cell voltage and often leads to parasitic reactions at electrode interfaces. Although neutral aqueous electrolytes offer excellent safety and chemical stability, their limited voltage window restricts the energy density of aqueous battery systems.

One promising strategy for overcoming this limitation involves the use of highly concentrated aqueous electrolytes, often referred to as water-in-salt systems. In such electrolytes, the high salt concentration significantly reduces the activity of free water molecules and alters the solvation structure of lithium ions. This modified solvation environment suppresses hydrogen and oxygen evolution reactions and enables operation at significantly higher voltages than those typically achievable in dilute aqueous systems.

Future research could therefore explore the compatibility of LTO anodes with various high-concentration electrolyte formulations, with particular attention to interfacial stability and long-term cycling behavior. Investigating how these electrolytes influence solid–electrolyte interphase formation, gas evolution kinetics, and electrode corrosion could provide valuable insight into the mechanisms that govern stability in aqueous battery systems. Such studies may also reveal opportunities to combine optimized electrolyte formulations with engineered electrode architectures to further expand the practical voltage window of aqueous lithium-ion batteries.

## 6.3 Toward LTO/LMO Aqueous Full Cells

While many studies focus on half-cell configurations to evaluate anode performance, the ultimate objective of aqueous battery research is the development of stable full-cell systems capable of practical energy storage. One of the most promising cathode candidates for pairing with LTO anodes in aqueous environments is lithium manganese oxide ($LiMn_2O_4$, LMO). The relatively high operating potential of LMO and its

compatibility with neutral aqueous electrolytes make it an attractive counterpart for constructing aqueous lithium-ion full cells.

Future work could therefore investigate the design and optimization of LTO/LMO aqueous full-cell architectures. Key parameters to be explored include electrode balancing, electrolyte composition, and electrode thickness ratios that maximize energy efficiency while maintaining long-term stability. Particular attention should be given to minimizing polarization losses and suppressing parasitic reactions at both electrodes.

In addition, the development of optimized electrode architectures could play a decisive role in improving full-cell performance. Controlling electrode porosity, particle connectivity, and electrolyte accessibility may help mitigate transport limitations that become more pronounced in full-cell configurations. By integrating optimized synthesis routes, advanced electrode fabrication strategies, and carefully engineered electrolyte systems, it may be possible to achieve aqueous battery systems that combine safety, stability, and competitive electrochemical performance.

## 6.4 Outlook

The results of this work suggest that the future development of ALIBs will depend on the coordinated optimization of multiple design parameters rather than isolated improvements in individual components. Advances in material synthesis, electrode architecture, and electrolyte chemistry must therefore be pursued simultaneously to fully exploit the advantages of aqueous electrochemical systems.

In particular, LTO-based electrodes represent a promising platform for investigating the interplay between structural stability, interfacial chemistry, and electrode fabrication techniques in aqueous environments. Continued research along these directions could lead to battery systems that retain the intrinsic safety and environmental benefits of aqueous electrolytes while approaching the performance levels required for practical large-scale energy storage.

Ultimately, the development of reliable ALIBs could contribute significantly to the broader transition toward safer and more sustainable electrochemical energy-storage technologies.