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Design and Recycling of Electrolytes for Next Generation Batteries

Focus on Calcium-Ion and Lithium-Ion based systems

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Abstract

This thesis explores the design and recycling of electrolytes for next-generation energy storage systems, focusing on two primary areas: the recycling of lithium iron phosphate (LiFePO_4) battery electrolytes and the design of multivalent calcium-ion electrolytes. The growing demand for efficient and sustainable energy storage solutions necessitates advancements beyond conventional lithium-ion systems, which face challenges such as limited resource availability and environmental impact.

Innovations in lithium-based electrolytes that incorporate end-of-life considerations and account for degradation during recycling, particularly under atmospheric exposure, are important for improving battery lifespan and sustainability. In parallel, calcium-ion technology emerges as a promising multivalent-ion alternative, representing a paradigm shift that combines improved energy density with superior material sustainability. Advancements in electrolyte design for calcium-ion batteries are essential to overcoming challenges related to ionic conductivity and electrochemical stability, enabling their practical implementation.

This research integrates experimental techniques such as Gas Chromatography-Mass Spectrometry (GC-MS), Raman spectroscopy, and Fourier Transform Infrared (FT-IR) spectroscopy with computational methods including Molecular Dynamics (MD) simulations and Density Functional Theory (DFT) calculations to investigate the electrochemical behavior, structural stability, and recyclability of these electrolytes. The findings provide methodological insights for the development of sustainable, high-performance electrolytes and support the integration of circular economy principles into future energy storage technologies.

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Chapter 1

Introduction

Chapter Overview

This chapter provides a comprehensive review of current lithium-ion battery technologies while introducing the emerging importance of multivalent-ion systems, with a particular focus on calcium-ion batteries. Electrolytes, as the medium for ionic transport, play a decisive role in determining energy density, cycle life, and safety. The discussion is structured around two complementary directions: first, addressing the sustainability challenges of lithium-ion batteries (LIBs) through the study and recycling of spent electrolytes; and second, exploring the development of calcium-ion battery (CIB) electrolytes as geopolitically resilient alternatives. Taken together, these approaches respond to systemic vulnerabilities in today's energy storage systems while remaining aligned with the principles of the circular economy. Accordingly, the first part of the chapter examines strategies to mitigate lithium scarcity and environmental risks through advanced electrolyte recycling, while the second part considers calcium-ion systems as a promising sustainable paradigm that demands tailored electrolyte innovations. The chapter concludes by outlining the thesis's research objectives, which unify the themes of electrolyte development for calcium-ion batteries and electrolyte recycling for lithium-ion systems. By integrating molecular simulations with spectroscopic and analytical techniques, the thesis establishes a common framework for understanding electrolyte structure and reactivity, forming the foundation for the investigations presented in the following chapters.

1.1 Fundamentals of Intercalation-Ion Batteries and the Central Role of the Electrolyte

Intercalation-ion batteries operate through a reversible intercalation mechanism in which charge carrier ions (such as Li^+ , Na^+ , Ca^{2+} , Mg^{2+} , ...) shuttle between the cathode and anode during charge and discharge. This process is enabled by a carefully engineered assembly of materials, including the anode, cathode, separator, and electrolyte, whose arrangement in a typical cell is shown in Figure 1.1. During charging, external energy drives the charge carrier ions from the cathode host structure into the anode, while electrons travel through the external circuit to maintain

charge neutrality. Upon discharge, this flow reverses, allowing the stored chemical energy to be delivered as electrical energy to a device or grid. The electrolyte provides the ion-conducting medium necessary for this shuttle mechanism, while the electronic insulation between electrodes prevents internal short circuits.

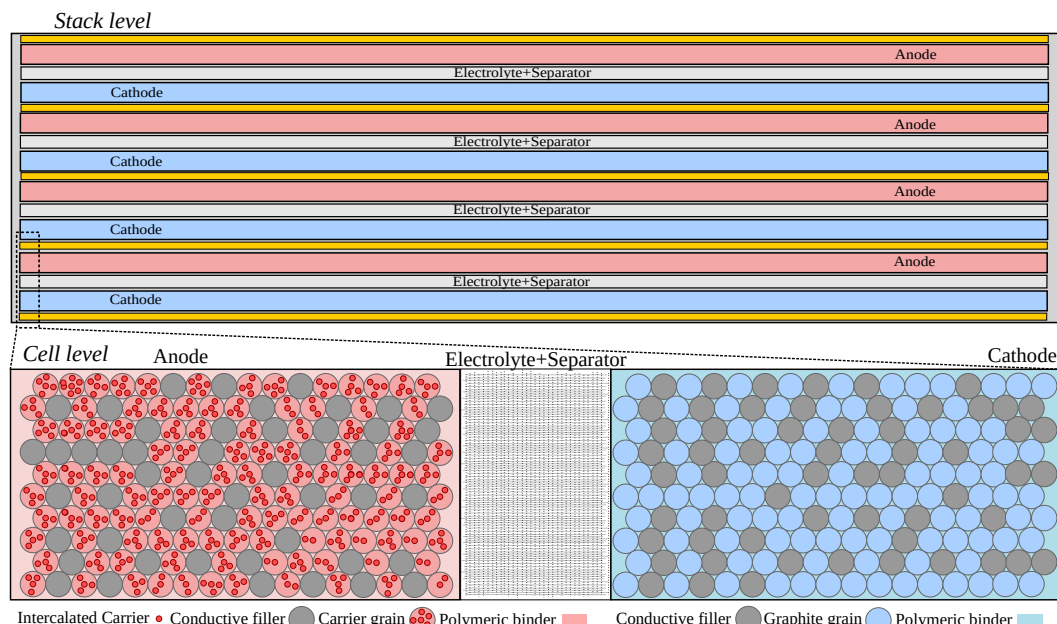


Figure 1.1 Schematic representation of the main components of an Intercalation-ion battery, including anode, cathode, separator, and electrolyte. The electrolyte ensures ionic conduction while electronically insulating the electrodes.

The charge–discharge mechanism, summarised in Figure 1.2, highlights how the electrolyte not only sustains ion transport but also governs the interfacial reactions that form passivation layers such as the solid electrolyte interphase (SEI) on the anode and the cathode electrolyte interphase (CEI) on the cathode. These interphases regulate ion insertion kinetics and long-term stability, meaning that small variations in electrolyte composition or degradation pathways can dramatically influence battery performance, safety, and lifetime.

A crucial aspect of electrolyte functionality lies in its ability to simultaneously dissolve the charge carrier salt, maintain high ionic conductivity, and remain electrochemically stable across the operating voltage window of the battery. However, electrolytes are inherently reactive environments that can degrade during cycling, producing soluble and volatile species that influence interphase formation, capacity retention, and overall safety. This sensitivity becomes even more pronounced as battery chemistries evolve beyond monovalent lithium systems.

Indeed, when moving from monovalent (such as Li^+ or Na^+) to multivalent charge carriers (such as Ca^{2+} or Mg^{2+}), the electrolyte challenge becomes substantially more complex. Multivalent ions possess higher charge density and stronger electrostatic interactions, which deepen their solvation shells, slow down diffusion, and increase the tendency to form tight ion pairs or aggregates. These effects demand electrolyte formulations with finely tuned solvation properties and carefully designed anion

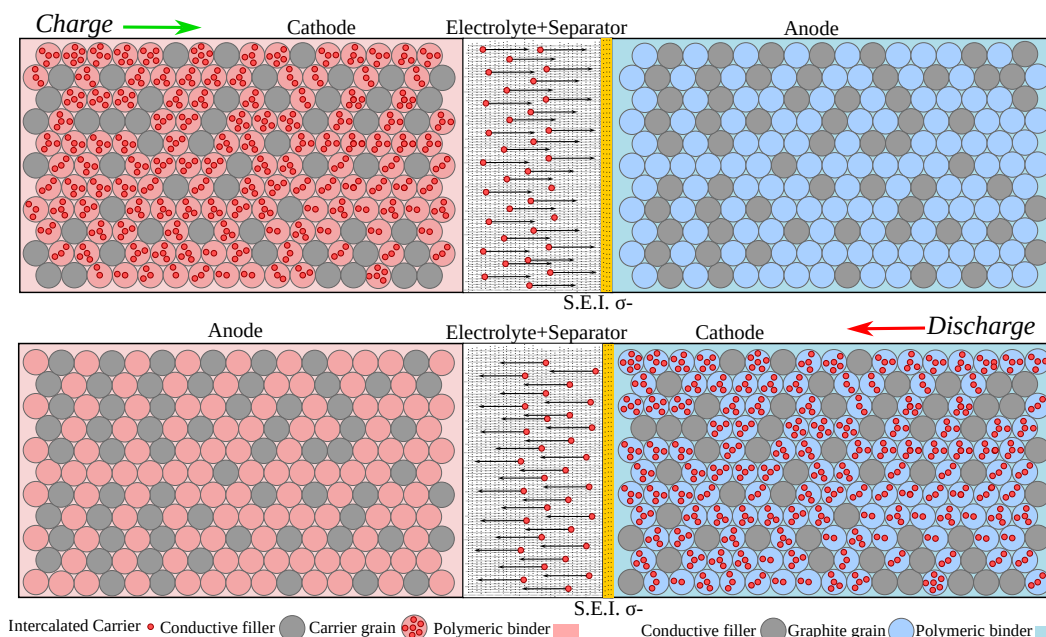


Figure 1.2 Illustration of the charge–discharge mechanism in an Intercalation-ion battery. The electrolyte mediates the charge carrier (Li^+ or Ca^{2+}) transport between the electrodes and participates in the formation of interphase layers that control performance and stability.

structures.

Classical electrolytes developed for LIBs often fail in this regard, as they lead to excessive ion pairing or interfacial passivation when used with multivalent metals. This comparison underscores why the study of electrolytes is central not only for optimizing current lithium-ion technologies but also for enabling next-generation systems based on more earth-abundant multivalent ions. Understanding electrolyte structure, stability, and reactivity, both during operation and at end-of-life, is therefore essential for advancing sustainable energy storage. Such understanding requires a combination of experimental techniques and computational tools capable of resolving solvation structure, ion aggregation, interphase chemistry, and degradation pathways at the molecular scale.

These considerations illustrate why electrolyte chemistry stands at the interface between battery performance, durability, and sustainability. A rigorous understanding of solvation structure, ion–solvent interactions, interfacial reactions, and degradation routes is therefore indispensable when comparing mature monovalent systems such as lithium-ion batteries with emerging multivalent technologies like calcium-ion batteries. The complexities introduced by multivalent charge carriers, together with the growing need to manage electrolyte degradation and recovery in established LIB chemistries, naturally motivate the detailed analytical and computational investigations developed throughout this thesis. The following sections build on this foundation by outlining the scientific context, challenges, and motivations that frame the work presented in the subsequent chapters.

1.2 Background

The sustainability of lithium-ion batteries (LIBs) faces critical challenges due to lithium scarcity, driven predominantly by rapidly growing demand for electric vehicles and renewable energy technologies [1, 2]. The shift towards renewable energy and electrified transportation is intensifying demand for LIBs, necessitating substantial lithium supply that significantly surpasses current extraction and recycling capacities [2]. Projections indicate that global lithium demand could potentially exceed available resources by 2025, creating an urgency for developing improved and sustainable extraction methods [3].

Current lithium extraction techniques involve processing minerals such as spodumene, extraction from brines, and recovery from spent LIBs [4]. Each method has distinct limitations. Spodumene processing requires high energy input and generates substantial waste, while chemical processing raises risks of contamination [3]. Conversely, lithium extraction from brines, notably in South America’s Salar regions, significantly impacts local water resources, leading to shortages in arid environments and broader ecological consequences such as biodiversity loss [3, 5].

Besides environmental concerns, lithium extraction also faces geopolitical and economic vulnerabilities. The uneven geographic distribution of resources, compounded by geopolitical tensions, leads to unstable supply chains and unpredictable market fluctuations [6, 7]. Furthermore, extraction activities often occur in regions with weaker environmental and labor regulations, raising ethical and sustainability concerns [3].

Electrolytes critically impact both the performance and recyclability of LIBs. Recent innovations in formulations such as ionic liquids and solid-state electrolytes significantly improve thermal stability, safety, and electrochemical performance compared to conventional carbonate-based systems [8]. Nanostructured electrolyte materials further enhance ionic conductivity and mechanical stability, mitigating issues such as degradation and flammability [8]. However, electrolyte recycling remains underdeveloped, despite electrolytes being a significant component of LIBs. Early approaches, including mechanical processing, solvent extraction, and supercritical CO₂ extraction, show promise but still face challenges in scalability, purity, and environmental management [9, 10].

Specific recycling challenges are also pronounced for lithium iron phosphate (LiFePO₄, LFP) cathodes, which are widely used due to their low cost and safety profile. These materials tend to degrade upon moisture exposure and interact unfavorably with electrolytes, complicating recovery processes [11, 12]. Contaminants such as residual aluminum and carbon further reduce the quality of regenerated materials, underscoring the need for advanced regeneration methods [13].

Alternative battery chemistries, such as calcium-ion batteries (CIBs), present viable options to reduce reliance on lithium, leveraging calcium’s abundance and affordability [14]. CIBs offer significant advantages, including higher volumetric energy density and potentially safer operation, particularly when employing solid-state or aqueous electrolytes [15, 16]. Aqueous electrolytes notably enhance safety, improve cycle life, and enable faster charging. For instance, polyimide-based anodes paired with aqueous electrolytes have shown promising long-term stability and capacity retention [16].

Despite these advantages, CIBs face substantial challenges. Ion mobility limitations and electrode compatibility hinder fast charge–discharge cycles [13, 14]. Divalent calcium ions diffuse more slowly than monovalent lithium, and achieving stable electrode–electrolyte interfaces remains essential to practical implementation. Recent studies highlight the role of innovative electrode structures, such as Prussian blue analogues, in addressing these issues [16, 17]. These interfaces must also resist passivation, a known challenge when calcium metal is used directly as an anode [13]. In conclusion, ensuring the sustainability of LIBs requires a multifaceted approach that integrates advanced recycling technologies, the development of alternative chemistries, and robust regulatory frameworks. Such a strategy can reduce environmental impacts, optimize resource use, and strengthen the resilience of global battery supply chains, thereby supporting the transition to clean and sustainable energy systems [5, 17]. Continued interdisciplinary research bridging materials science, environmental policy, and industrial engineering will be essential to achieving these sustainability goals.

Within this context, understanding the degradation behavior and recyclability of LIB electrolytes becomes particularly critical. Electrolytes not only govern ion transport and interfacial stability during operation but also account for a significant fraction of battery mass, making their end-of-life management a central challenge for both performance and sustainability.

1.3 Electrolyte Challenges in Lithium-Ion Batteries

Lithium-ion battery (LIB) electrolyte degradation results from a complex interplay of chemical, mechanical, and thermal mechanisms that predominantly involve electrode–electrolyte interphase formation and bulk electrolyte decomposition. These degradation pathways lead to capacity fade, power loss, and elevated internal resistance, ultimately shortening battery lifespan [18, 19]. Electrolyte stability is therefore crucial for maintaining efficient ion transport and stable electrode interfaces during operation. Commonly used carbonate-based electrolytes such as dimethyl carbonate (DMC)-LiPF₆, ethyl methyl carbonate (EMC)-LiPF₆, and diethyl carbonate (DEC)-LiPF₆ undergo thermal degradation, which decreases ionic diffusivity through the formation and clustering of decomposition byproducts [20]. Advanced analytical techniques including gas chromatography–mass spectrometry (GC-MS) and nuclear magnetic resonance (NMR) spectroscopy have revealed that degradation primarily stems from electrochemical reduction of linear alkyl carbonates (DMC, EMC, DEC), whereas cyclic carbonates like ethylene carbonate (EC) contribute minimally [21]. Characterization of electrolyte degradation has been greatly advanced by a combination of analytical and spectroscopic methods. For liquid electrolytes, techniques such as GC-MS and NMR provide detailed insights into solvent and additive transformations as well as lithium salt breakdown in aged cells, enabling a granular understanding of chemical evolution during cycling [18]. In contrast, solid electrolytes, particularly sulfide-based argyrodite types, suffer from moisture-induced degradation, producing toxic hydrogen sulfide and impairing lithium-ion conductivity. To investigate these effects, diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) has been instrumental in elucidating moisture-driven structural changes

and recovery mechanisms under controlled heat treatments [22]. Together, these complementary analytical approaches bridge molecular-level insights with practical implications for battery longevity and safety.

The interphase films formed at electrode–electrolyte interfaces, namely the solid electrolyte interphase (SEI) on anodes and the cathode electrolyte interphase (CEI) on cathodes, are critical to electrolyte stability. These layers, while protective, evolve dynamically during cycling and irreversibly consume electrolyte components. In this context, the increasing use of nanocomposite electrodes, valued for their high capacity and performance, adds further complexity. Their large surface area and structural defect sites can intensify electrolyte decomposition, leading to accelerated side reactions and the generation of diverse degradation products. Compounds such as lithium methyl carbonate and ethylene oxide oligomers have been detected by GC–MS [23]. The accumulation of such species thickens the interphases, hinders lithium-ion transport, and hastens capacity loss. From a recycling perspective, these degradation pathways reduce the recoverable fraction of the electrolyte and complicate purification strategies, underscoring the importance of understanding electrode-induced electrolyte instability.

Environmental and operational conditions also profoundly impact degradation kinetics. For instance, elevated temperatures accelerate electrolyte decomposition but can also promote protective LiF-rich CEI formation in concentrated electrolytes, mitigating further breakdown and preserving cathode integrity [24]. Building on this understanding, optimized formulations that tune lithium salt concentration, solvent volatility, and additive composition have expanded the operational temperature window of LIBs to $-40\text{ }^{\circ}\text{C}$ to $60\text{ }^{\circ}\text{C}$, a range crucial for applications from cold climates to hot environments [25, 26].

Beyond liquid and solid electrolytes, polymer electrolytes have emerged as promising alternatives that address both degradation and sustainability challenges. Despite inherent limitations such as lower ionic conductivity and poor electrode interfacial compatibility, advances in crosslinked polymer networks, inorganic fillers, and plasticizers have substantially improved performance [27]. Common hosts such as polyethylene oxide (PEO), polyacrylonitrile (PAN), and polyvinylidene fluoride (PVDF) provide mechanical robustness and thermal stability while enabling lithium-ion transport when suitably modified. Importantly, the tunability and recyclability of polymer and gel electrolytes offer sustainable pathways for LIB systems capable of withstanding harsh cycling and environmental conditions.

Recycling of LIB electrolytes is pivotal for both economic viability and environmental protection. Since electrolytes constitute 10–15% of battery weight and contain valuable lithium salts and organic solvents, their recovery alleviates raw material scarcity and reduces environmental hazards [10, 28]. However, conventional pyrometallurgical recycling incinerates electrolytes, releasing toxic fluorinated compounds and disregarding their resource value [28]. By contrast, hydrometallurgical and electrochemical recovery approaches, including solvent extraction and supercritical CO_2 techniques, provide more sustainable pathways, though challenges remain regarding scalability, selectivity, and purity control [9, 29].

Recent progress in direct regeneration and hydrometallurgical leaching has demonstrated promising efficiency in recovering lithium and other elements from degraded LiFePO_4 cathodes, thereby contributing to a more integrated recycling ecosystem

[11, 30]. In parallel, solution-precipitation methods enhance recovery yields while minimizing secondary pollution, reducing the environmental footprint of recycling operations [30, 31]. Crucially, cathode recovery processes are now increasingly coordinated with the identification and separation of electrolyte degradation products, underscoring the interdependence of cathode and electrolyte recycling. Sustainable strategies also target minimization of toxic fluoride emissions, a major concern in hydrometallurgical processing.

Innovations focused on capturing and converting fluoride species into benign compounds are essential to mitigate soil and air contamination [10, 32]. Complementing these technological advances, integration of life cycle assessment (LCA) and techno-economic analysis (TEA) frameworks enables evaluation of environmental and economic impacts across recycling pathways, thereby guiding the development of cost-effective and sustainable technologies [5, 29].

In summary, LIB electrolyte degradation is a multifaceted phenomenon driven by intricate interfacial and bulk processes. To unravel these complexities, spectroscopy, mass spectrometry, and electrochemical techniques provide critical mechanistic insights that guide electrolyte formulation and interface engineering. Building on this foundation, advances in polymer and ionic liquid electrolytes offer promising routes to improve thermal and mechanical stability, addressing degradation while extending operational windows. In parallel, recycling technologies are rapidly evolving to achieve high recovery efficiency with environmental and economic feasibility. Ultimately, a holistic approach that integrates material innovation, mechanistic understanding of degradation, and sustainable recycling will be key to advancing LIB performance and enabling true circularity in energy storage.

1.4 Importance of Multivalent-Ion Systems

Multivalent-ion batteries represent a transformative advance in energy storage technologies, aiming to overcome the intrinsic limitations of lithium-ion systems by exploiting charge carriers capable of transferring multiple electrons per ion. This fundamental property enables ions such as Ca^{2+} , Mg^{2+} , Zn^{2+} , and Al^{3+} to deliver higher theoretical capacities and energy densities, while offering potential advantages in cost, safety, and elemental abundance [33, 34]. Although lithium-ion batteries (LIBs) currently dominate the market, concerns over resource scarcity, rising costs, and supply vulnerabilities have intensified research into alternative chemistries, with calcium-ion batteries (CIBs) emerging as particularly promising [35, 36].

Calcium stands out among multivalent ions due to its natural abundance, low cost, and favorable electrochemical properties. Its divalent nature theoretically doubles the charge capacity per ion compared to lithium, while its redox potential (-2.87 V vs. SHE) closely approaches that of lithium (-3.04 V vs. SHE), enabling operation over wide voltage windows [14, 37]. Moreover, compared to magnesium or aluminum, calcium exhibits lower charge density and polarization strength, translating into enhanced ionic mobility and reduced structural disruption during intercalation [35, 36].

Despite these advantages, practical realization of CIBs faces formidable challenges. Chief among them are the sluggish solid-state diffusion kinetics of Ca^{2+} in cathode

hosts, complex interfacial chemistry at the calcium metal anode, and the development of stable, compatible electrolytes [13, 38]. Calcium’s large ionic radius and strong electrostatic interactions hinder mobility in layered oxides, leading to poor rate capability and capacity fading [36, 39]. In parallel, the high reactivity of calcium metal promotes the growth of passivating surface films during plating/stripping, which block ion transport and severely limit Coulombic efficiency and cycle life [14, 35].

Electrolyte design has therefore emerged as a critical determinant of CIB performance. Early studies showed that many conventional salts and solvents decompose rapidly at calcium interfaces, forming insulating layers that inhibit transport [40, 41]. Recent advances point to bulky, weakly coordinating anions (TFSI⁻, BF₄⁻, TFO⁻, carboranes) and high-permittivity solvents (EC, PC, glymes) as promising options, with glymes particularly stable at calcium surfaces [40, 41]. Ab initio molecular dynamics simulations further revealed that calcium closo-monocarborane salts in tetra-glyme solvent exhibit minimal reductive decomposition compared to the rapid breakdown of PF₆⁻ and TFSI⁻ in carbonate media [40]. Experimentally, salts such as Ca[BF₄]₂ and Ca[BH₄]₂ in ether solvents have enabled reversible calcium plating/stripping, although their anodic stability and compatibility with high-voltage cathodes remain limited [42, 43].

Progress has also been made in cathode development. Prussian blue analogues (PBAs) with open frameworks facilitate Ca²⁺ diffusion and show good stability, particularly in aqueous systems [13, 36]. Layered oxides such as V₂O₅, CaCo₂O₄, and molybdenum oxides have been explored by tuning interlayer spacing and morphology [36]. More recently, dual-carbon batteries employing graphitic anodes and cathodes demonstrated high operating voltages (4.6 V) and long-term cycling in carbonate electrolytes, leveraging reversible co-intercalation of Ca²⁺ and anions [42].

Nevertheless, the interfacial challenges of calcium metal anodes remain severe. Unlike the beneficial SEI in LIBs, insulating layers formed on Ca are impermeable to Ca²⁺, causing irreversible capacity loss and poor efficiency [40]. Approaches under investigation include artificial interphases, electrolyte additives promoting Ca²⁺-conductive SEI, or replacing metallic calcium with alloying or intercalation-type anodes [35, 41].

Finally, the solvation structure of Ca²⁺ strongly influences transport and power performance. Ion pairing and aggregation raise desolvation energies and hinder charge transfer. Studies show that solvation depends on salt concentration, solvent donicity, and anion identity, with carbonate solvents promoting extensive ion pairing [41]. Engineering electrolytes to optimize solvation and minimize aggregation is therefore key to improving kinetics and conductivity.

In summary, while calcium-ion batteries face major obstacles in electrolyte stability and interfacial chemistry, recent experimental and computational advances have significantly expanded mechanistic understanding and guided rational materials design [38, 40]. Continued interdisciplinary efforts targeting new salts and solvents, engineered interphases, and advanced electrode materials will be essential to unlock the full potential of CIBs as sustainable, high-performance energy storage systems [33, 35].

1.5 Electrolyte Recycling Challenges

Beyond electrode recycling, electrolyte recovery emerges as a critical yet underdeveloped component of sustainable battery technologies. Electrolytes contain both hazardous organic solvents and valuable lithium salts that are essential to battery operation and economically attractive to recover [29, 44]. As global demand for LIBs accelerates, driven by electric vehicles and renewable energy storage, the development of efficient and environmentally benign recycling strategies has become urgent [45]. However, despite substantial advances in cathode and anode recycling, electrolyte recovery remains technically challenging and a bottleneck to achieving a circular battery economy [46, 47].

Current recycling technologies include mechanical processing, thermal distillation, solvent extraction, and more recently supercritical CO₂ (scCO₂) extraction [44, 48]. Mechanical routes liberate electrolytes through crushing and separation, but removal is often incomplete and can damage active materials [46]. Distillation exploits solvent volatility but requires high energy input and risks generating secondary pollutants [47]. Solvent extraction improves lithium salt recovery but raises concerns over solvent management and environmental trade-offs [44]. In contrast, scCO₂ extraction combines tunable solvation power with low environmental impact, enabling efficient removal while preserving electrode integrity [47, 49].

Hydrometallurgical and pyrometallurgical recycling, delivering metal recovery efficiencies of 75% and 85%, respectively, indirectly affect electrolytes by altering residual organics and decomposition products [44, 48]. Innovations such as deep eutectic solvents (DESs), molten salt roasting, and bioleaching are under exploration to boost recovery while reducing environmental burdens [47, 49]. Electrochemical techniques, including electrosorption and electrodialysis, show promise for selective lithium salt separation with minimal waste, though electrode durability and membrane selectivity remain challenges [12, 49].

Advanced analytical methods are critical to optimize these processes. X-ray diffraction (XRD) reveals structural degradation and impurity phases (e.g., AlPO₄) in recycled LiFePO₄, guiding targeted purification [50, 51]. Complementary FT-IR spectroscopy and GC-MS detect organic decomposition products, enabling tighter process control [52, 53]. Such multimodal characterization is essential for tailoring recycling protocols and for anticipating the even more complex chemistries of multivalent-ion systems [44].

The economic case for recycling is also compelling. In China, projections estimate that recycling 11.77 million tons of spent LIBs by 2035 could generate over 40.5 \$ billion, with cobalt and lithium recoveries contributing 8.2 \$ and 4.3 \$ billion, respectively [54, 55]. State-of-the-art facilities already report recovery efficiencies of 95% for graphite, 90% for lithium, and 85% for cobalt, demonstrating the viability of integrated recycling [55]. Environmentally, direct closed-loop recycling of production scrap reduces cumulative energy demand and greenhouse gas emissions by reusing electrodes without full breakdown and re-synthesis [5, 56].

Nevertheless, scaling and standardizing these processes remains difficult. The diversity of cell chemistries, form factors, and aging states complicates disassembly and pretreatment, requiring adaptable and robust process designs [57, 58]. Moreover, electrolyte recycling must be future-proofed to address next-generation chemistries

such as calcium-ion batteries (CIBs).

In CIBs, electrolyte degradation, particularly of carbonate solvents like ethylene carbonate, produces resistive interphases of CaCO_3 and CaO , which block reversible plating/stripping and complicate recycling [59, 60, 61]. Proposed solutions include artificial SEI coatings and gel polymer electrolytes (GPEs). Artificial SEIs stabilize electrode surfaces, reducing parasitic reactions and simplifying recycling streams, while GPEs enhance Ca^{2+} transport, suppress dendrites, and extend cycle life [61]. Together, these strategies improve both performance and recyclability by preserving electrode integrity and ensuring cleaner, higher-purity material recovery.

Stabilizing electrode–electrolyte interfaces not only enhances battery performance but also reduces contamination and phase heterogeneity at end of life, facilitating more scalable recycling [44, 61]. Lessons from LiFePO_4 recycling, such as impurity detection by XRD and hydrothermal regeneration, provide valuable models, though calcium’s unique chemistry requires tailored approaches [12, 13, 29].

A circular economy perspective emphasizes hybrid recycling chains that integrate mechanical, hydrometallurgical, and pyrometallurgical steps to maximize recovery [62]. While pyrometallurgy robustly retrieves metals, it overlooks organics and electrolytes, making pre-treatment and chemical leaching essential for recovering lithium salts and solvents [63]. Recycling efficiency also hinges on precise dismantling and sorting, which improve downstream yields and minimize environmental impacts [62].

Advanced in situ techniques further refine recycling. Neutron diffraction and XPS studies on $\text{LiFePO}_4/\text{FePO}_4$ hybrids revealed lithium loss and phase segregation, guiding chemical compensation strategies that restore pristine structures and performance [50]. Such insights enable energy-efficient recycling methods that avoid harsh acids/alkalis and lower greenhouse emissions.

In summary, advancing electrolyte recycling is vital for sustainable resource management, environmental protection, and economic viability of LIBs and emerging multivalent-ion batteries [47]. Continued progress in analytical tools, eco-friendly processes, and interfacial stabilization will be decisive in closing the battery lifecycle loop. The interplay between LIB and CIB research offers unique opportunities for cross-disciplinary innovation, ultimately supporting a resilient and sustainable global energy storage infrastructure [29, 44, 61].

1.6 Research Objectives

This thesis addresses two complementary challenges at the core of next-generation battery development: the design of advanced electrolytes for emerging calcium-ion batteries (CIBs) and the sustainable recycling of spent electrolytes in lithium-ion batteries (LIBs). Although these two research directions belong to different stages of a battery’s life, electrolyte formulation for CIBs and end-of-life management for LIBs, they are united by a common scientific ambition: to understand how electrolyte structure, stability, and reactivity evolve under operating conditions and how this knowledge can be harnessed both to engineer improved performance and to enable responsible, circular-economy practices.

In the first part of the thesis, the focus is placed on calcium-ion batteries, where

the fundamental objective is the rational design of functional electrolytes capable of supporting efficient Ca^{2+} transport and stable electrode–electrolyte interfaces. Achieving this goal requires an accurate description of calcium solvation, ion pairing, and concentration-dependent structural evolution. To this end, the thesis apply and develops dedicated classical and polarizable force-field parameters for Ca^{2+} , bis(trifluoromethanesulfonyl)imide (TFSI⁻), and propylene carbonate (PC) directly within this work, enabling molecular dynamics (MD) simulations that capture the intricacies of multivalent ion coordination. These simulations, together with density functional theory (DFT) calculations of representative solvation clusters, provide a microscopic understanding of electrolyte behavior that is validated experimentally through Raman spectroscopy. This integrated approach allows the research to determine how electrolyte composition influences solvation structure and how these structural features correlate with transport properties and stability.

The second part of the thesis shifts attention to lithium-ion battery technology, with the aim of elucidating electrolyte degradation mechanisms and identifying pathways for electrolyte valorization and recycling. In this part, all materials investigated, except for the electrolyte itself, are sourced from recycled LIB cells, ensuring that the study reflects realistic industrial end-of-life conditions. The objective is not only to identify degradation products and their evolution during cycling but also to determine under which conditions the electrolyte or its components can be recovered or re-utilized. This is accomplished by combining experimental techniques such as Fourier Transform-Infrared (FT-IR) spectroscopy and Gas Chromatography-Mass Spectrometry (GC-MS) with MD and DFT calculations that assist in assigning vibrational signatures and interpreting fragmentation pathways. Across both research directions, the thesis adopts a unified methodology in which computed data (from MD and DFT) and analytical data (from Raman and FT-IR spectroscopy, and GC-MS) are used synergistically to construct a coherent and consistent molecular picture of the systems under study. MD simulations provide time-resolved insight into solvation structures, ion association, and electrolyte reorganization; DFT calculations elucidate the stability, energetics, and vibrational signatures of representative coordination environments; Raman spectroscopy offers experimental validation of solvation motifs through their characteristic vibrational fingerprints; FT-IR complements Raman by probing functional-group evolution and detecting changes in electrolyte composition with high sensitivity; and GC-MS identifies and quantifies volatile species formed during degradation. Together, these computational and experimental tools allow the thesis to determine not only what structural motifs and degradation products arise in the electrolytes, but also why they form, how they evolve under operating conditions, and in what ways they influence ion transport, electrolyte stability, and recyclability.

Overall, the objectives of this thesis are achieved by demonstrating that electrolyte design for calcium systems and electrolyte recycling for lithium systems can be understood through a common physico-chemical framework based on molecular structure, vibrational signatures, and reactive pathways. The answers formulated throughout the work establish that accurate force-field development, multiscale modelling, and targeted analytical characterization together provide a powerful toolkit for interpreting electrolyte behavior and guiding the development of sustainable energy-storage technologies.

Chapter 2

Methods

Chapter Overview

This chapter presents the theoretical and experimental methods used to investigate electrolytes for next-generation batteries. Computational approaches, including molecular dynamics simulations and density functional theory, provide atomistic insight into solvation environments and structural organization. These simulations are complemented by vibrational spectroscopy (Raman and Infrared) and gas chromatography–mass spectrometry, which are employed to characterize electrolyte composition and monitor its evolution under operating conditions. The chapter discusses each method individually, highlighting its theoretical background, practical implementation, and specific application to electrolyte characterization and analysis. Together, these approaches establish a comprehensive methodological framework that supports the interpretation of the results presented in subsequent chapters.

2.1 Molecular dynamics simulations

Molecular dynamics (MD) offers a deterministic, atomistic framework to investigate the evolving structure of liquid battery electrolytes. By integrating Newton's equations of motion for interacting nuclei, MD generates time-ordered trajectories that represent statistically valid microstates of an N-body system. Simulations apply periodic boundary conditions to approximate bulk behavior and advance through time steps small enough to resolve high-frequency vibrations while accessing nanosecond-scale relaxation. Thermostat–barostat coupling ensures proper ensemble sampling of thermodynamic phase space.

Structural characterization relies on trajectory-derived correlation functions. The radial distribution function (RDF) reveals ion–solvent ordering, with the first maximum identifying coordination distances and the first minimum defining solvation shell boundaries. This distinction enables identification of contact ion pairs versus solvent-separated configurations.

Achieving statistical convergence for electrolyte systems requires carefully designed protocols, including energy minimization, ensemble-constrained equilibration, and extended production runs to sample rare events such as ion clustering. Finite-size artifacts are mitigated using particle-mesh Ewald methods, which preserve the in-

tegrity of long-range Coulomb interactions across periodic boundaries [64].

These structural descriptors directly connect atomistic organization with electrochemical performance: shorter cation–anion separations are often associated with reduced ionic mobility in electrolyte systems, while pronounced solvent layering around cations predicts higher desolvation barriers at electrode interfaces [65]. MD thus provides a direct mapping from molecular arrangements to transport-relevant length scales, complementing ensemble-averaged spectroscopic techniques.

Building on the general framework of molecular dynamics, classical MD operates at an approximate level where atoms are treated as point masses interacting through predefined potential functions. All interactions are condensed into classical force fields, which parameterize bonded contributions, bond stretching, angle bending, torsions, and nonbonded interactions such as van der Waals and Coulombic terms. Within this Newtonian scheme, quantum electronic effects are neglected, but the efficiency gained enables simulations of large electrolyte systems over nanosecond to microsecond timescales.

A widely adopted implementation is the OPLS All-Atom (OPLS-AA) force field [66, 67], extensively parameterized for organic solvents used in electrolytes. Its formulation rigorously combines *ab initio* quantum calculations with empirical fitting to condensed-phase properties, ensuring balanced descriptions of both intra- and intermolecular interactions [68]. Torsional parameters, for example, were optimized against high-level rotational energy profiles of diverse organic molecules, reproducing conformational energetics with mean deviations below 0.2 kcal/mol. The breadth of functional group coverage: amines, ethers, sulfides, and aromatics, supports transferability across the wide chemical space of battery electrolytes.

Specialized extensions developed for ionic species, including hexafluorophosphate, triflate and bistriflylimide anions, further broaden its applicability to ionic liquids and complex electrolyte mixtures [69, 70].

Validation against experimental data has shown that OPLS-AA accurately reproduces densities, heats of vaporization, and structural features such as solvation shells, typically within a few percent of experimental values. This predictive power enables reliable estimation of diffusion coefficients and ion transport properties, making it a widely adopted framework for electrolyte modeling in battery research [71].

Nevertheless, classical force fields such as OPLS-AA inherit intrinsic limitations. Electrostatics are described using fixed partial charges that cannot adapt to local polarization environments, often leading to overestimated ion pairing and coordination strength. To mitigate this, empirical charge scaling (typically 0.7–0.9) is commonly applied, improving first-shell solvation and transport predictions but sometimes introducing artifacts beyond the primary shell and reducing transferability across compositions [72, 73, 74]. Similarly, harmonic approximations for bond and angle terms, and cosine expansions for torsions, may inadequately capture anharmonic effects in certain molecular species.

Despite these challenges, classical MD with OPLS-AA remains indispensable for probing solvation, ion transport, and structural organization in organic electrolytes. Its computational efficiency, broad parameterization, and compatibility with ion-specific extensions [75, 76] provide a powerful platform for high-throughput screening and mechanistic insight.

Building on this foundation, polarizable molecular dynamics (PMD) extends the clas-

sical framework by explicitly incorporating electronic polarization through induced dipoles or fluctuating charges that dynamically respond to the evolving electrostatic environment [77, 78]. This refinement is particularly crucial for battery electrolytes, where dielectric conditions fluctuate rapidly due to ion motion, solvent reorientation, and interfacial reactions.

Among the most advanced polarizable frameworks is the AMOEBA (Atomic Multipole Optimized Energetics for Biomolecular Applications) force field. AMOEBA extends classical electrostatics by combining permanent atomic multipoles (up to quadrupoles) with self-consistently induced dipoles, stabilized through Thole-type damping to prevent short-range over-polarization [78, 79]. Its parametrization integrates high-level quantum calculations with experimental condensed-phase data, yielding physically meaningful and transferable interaction models.

Recent applications have tailored AMOEBA to electrolyte systems containing glyme solvents and both alkali and multivalent cations. Hybrid parameterization strategies, combining force-matching, distributed multipole analysis, and molecular polarizabilities, have enabled accurate reproduction of experimental densities, dielectric constants, and ion-pairing energies in complex mixtures [80]. Importantly, AMOEBA simulations capture metal-ion coordination environments with high fidelity, including lithium and calcium, validating the role of multipolar electrostatics in low-permittivity environments relevant to battery research.

The many-body polarization treatment improves predictions of diffusion coefficients, ionic conductivity, and solvation structure compared to fixed-charge models, which often misrepresent ion aggregation [81]. AMOEBA further incorporates refined bonded terms, including anharmonic bond stretching, cross-angle coupling, and torsional potentials from quantum benchmarks, that enhance conformational flexibility and intramolecular polarization, both critical in multicomponent electrolytes.

The primary trade-off of PMD lies in computational cost: solving polarization equations at each timestep is substantially more demanding than classical MD. However, algorithmic advances and optimized implementations, notably in Tinker-HP, have extended the accessible system sizes and timescales [82]. As a result, polarizable MD now enables atomistic insights into solvation, mobility, and phase behavior that were previously inaccessible, offering a systematically improvable pathway toward realistic electrolyte modeling.

2.2 Density Functional Theory calculations

Density Functional Theory (DFT) has become an indispensable tool in computational chemistry, offering a unique balance between accuracy and computational cost for studying molecular and condensed-phase systems [83]. Unlike wavefunction-based methods, DFT describes the electronic structure through electron density, avoiding the explicit treatment of the many-electron wavefunction. This simplification makes DFT particularly well suited for probing complex molecular clusters, such as the first solvation shells of ions in battery electrolytes [84, 85].

In battery research, the first solvation shell refers to the ensemble of solvent molecules directly coordinating to an ion carrier, such as lithium or calcium. These molecules critically determine ion mobility, stability, and overall electrolyte performance

[86, 87, 88]. Accurate electronic-level characterization of such solvation environments is therefore essential for the rational design of next-generation electrolytes that enhance efficiency and durability.

The reliability of DFT calculations depends critically on the combined choice of exchange–correlation functional and basis set, as together they determine the accuracy with which electronic interactions are represented. Traditional functionals and modest basis sets often struggle to balance short-range chemical bonding with long-range dispersion forces, both of which are essential for correctly describing solvation shells in electrolyte environments.

Among modern functionals, ω B97X-D has emerged as a method of choice for ion–solvent systems [89]. Its range-separated hybrid formulation distinguishes between short- and long-range exchange effects, enabling precise treatment of localized interactions near solvated ions while capturing the diffuse electron correlation responsible for dispersion forces between solvent molecules. A built-in empirical dispersion correction further enhances its performance by realistically modeling van der Waals interactions that stabilize solvent coordination environments. Importantly, the functional also mitigates self-interaction errors common in charged systems by incorporating a significant fraction of long-range exact exchange from Hartree–Fock theory. These refinements yield more accurate electronic distributions and energy predictions, a necessity since even small inaccuracies may lead to qualitatively different conclusions about solvation shell stability or coordination geometry.

Complementing the functional choice, the Def2-TZVP basis set provides the mathematical framework for describing electron density with both flexibility and precision [90]. Belonging to the Def2 family of Gaussian-type orbital basis sets, it was designed to maximize accuracy and transferability across the periodic table while keeping computational costs manageable. Its triple-zeta valence plus polarization (TZVP) construction allows valence electrons to be represented by multiple functions, while polarization functions enable the wavefunction to adapt to the anisotropic interactions characteristic of solvation shells, such as ion–dipole alignment or hydrogen bonding. This adaptability improves the representation of solvent orientations around ions, improving predictions of stability and structure in solvated clusters.

The systematic and balanced design of Def2-TZVP minimizes basis set incompleteness errors and delivers reliable results for energies and geometries across diverse elements and compounds. Despite higher costs for large systems or heavy elements, where effective core potentials may be needed, Def2-TZVP remains a leading choice for electrolyte studies and a robust basis for high-quality DFT simulations.

Together, ω B97X-D and Def2-TZVP provide a state-of-the-art combination that balances accuracy and efficiency, enabling predictive modeling of solvated ion clusters in battery electrolytes. Their synergy allows computational results to align closely with experimental spectroscopy and molecular dynamics, yielding deep insight into solvation dynamics and ion transport mechanisms.

2.3 IR and Raman spectra simulation with DFT

The simulation of vibrational spectra, such as Raman and infrared (IR) spectroscopy, represents a powerful application of density functional theory (DFT), providing

detailed insight into molecular structure, dynamics, and intermolecular interactions. While FT-IR spectroscopy probes changes in dipole moment during vibrational motion, Raman spectroscopy is sensitive to variations in molecular polarizability. Accurate theoretical modeling of these spectra not only facilitates interpretation of experimental data [91], but also enables the elucidation of complex solvation environments in battery electrolytes.

At the methodological core, vibrational spectra simulations proceed through geometry optimization, which locates the equilibrium structure on the potential energy surface, followed by evaluation of the Hessian matrix to determine normal modes and harmonic frequencies. IR intensities are derived from the derivatives of the dipole moment along these vibrational coordinates, whereas Raman intensities arise from derivatives of the polarizability tensor. Together, these properties capture how molecules interact with electromagnetic radiation in the vibrational regime.

The accuracy of computed frequencies and intensities depends strongly on the chosen functional and basis set. Range-separated hybrid functionals such as ω B97X-D, supplemented with empirical dispersion corrections, improve predictions by correcting self-interaction errors and better representing weak noncovalent forces that shape solvation shells. Nevertheless, most calculations rely on the harmonic approximation, which assumes small displacements about equilibrium and neglects anharmonic effects, typically leading to systematic frequency overestimations.

To address these limitations, scaling factors are applied to the computed harmonic frequencies, usually derived from benchmark comparisons with experimental data. Temperature effects and instrumental resolution can be incorporated by convoluting the calculated stick spectra with line-broadening functions, yielding more realistic spectral profiles.

In practice, the computational workflow for solvated ion clusters follows a well-defined sequence: (i) geometry optimization under tight convergence criteria, (ii) frequency analysis to confirm the absence of imaginary modes, (iii) calculation of IR and Raman intensities via dipole and polarizability derivatives, and (iv) application of scaling and broadening corrections. The resulting spectra are then compared with experimental Raman and FT-IR data to validate the model and refine methodological choices.

Applied to battery electrolytes, this protocol provides molecular fingerprints of solvation environments. Vibrational spectra reflect subtle variations in coordination number, solvent orientation, and ion-solvent interaction strength, thereby revealing mechanistic details of ion transport, electrolyte stability, and solvation structure. In this way, Raman and IR simulations support both the rational design of advanced electrolytes and the interpretation of complex vibrational spectra observed experimentally.

2.4 Vibrational Spectroscopy in Electrolyte Characterization for Batteries

Vibrational spectroscopy represents a pivotal technique for probing molecular structure and dynamics by measuring vibrational transitions within molecules. Vibrational modes arise from the quantized motions of atoms around their equilibrium positions,

with frequencies determined by atomic masses and interatomic forces. For a molecule of N atoms, there are $3N - 6$ fundamental vibrational degrees of freedom (or $3N - 5$ for linear molecules). These vibrations correspond to discrete energy levels separated by quantized gaps, typically accessible in the infrared (IR) and visible spectral ranges.

The vibrational frequency $\tilde{\nu}$ (in cm^{-1}) of a diatomic bond, a fundamental building block of molecular vibrations, is classically approximated by:

$$\tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{f}{\eta}}, \quad (2.1)$$

where f is the effective bond force constant, η is the reduced mass of atoms with masses m_1 and m_2 , and c is the speed of light. This frequency corresponds to the energy gap between vibrational levels in the harmonic oscillator approximation. Quantum mechanically, the vibrational energy levels are given by:

$$E_v = hc\tilde{\nu} \left(v + \frac{1}{2} \right) - hc\tilde{\nu}x_e \left(v + \frac{1}{2} \right)^2 + \dots, \quad (2.2)$$

where $v = 0, 1, 2, \dots$ is the vibrational quantum number and x_e is the anharmonicity constant accounting for deviations from perfect harmonic behavior. Anharmonicity introduces overtones and combination bands, enriching the spectral information beyond fundamental transitions.

Among vibrational spectroscopic methods, Raman spectroscopy plays a central role thanks to its sensitivity to changes in molecular polarizability. Raman scattering is based on the inelastic scattering of monochromatic light: when incident photons interact with molecular vibrations, a small fraction is scattered with an energy shift corresponding to vibrational energies, an effect known as the Raman effect. The key physical quantity here is the molecular polarizability, which quantifies how the electron cloud distorts under an external electric field. The induced dipole moment $\mathbf{m}_0$ caused by the incident electric field $\mathbf{E}$ is:

$$\mathbf{m}_0 = \boldsymbol{\alpha} \cdot \mathbf{E}, \quad (2.3)$$

where $\boldsymbol{\alpha}$ is the polarizability tensor. Because vibrations modulate molecular geometry, polarizability varies with the vibrational normal coordinate Q_k , expandable near equilibrium as:

$$\boldsymbol{\alpha} = \boldsymbol{\alpha}_0 + \sum_k \left(\frac{\partial \boldsymbol{\alpha}}{\partial Q_k} \right)_0 Q_k + \dots, \quad (2.4)$$

with $\left(\frac{\partial \boldsymbol{\alpha}}{\partial Q_k} \right)_0$ governing the Raman activity of mode k . The differential Raman scattering cross-section, which determines the scattering intensity, is proportional to:

$$\frac{d\sigma}{d\Omega} \propto \nu_0^4 \left| \left(\frac{\partial \boldsymbol{\alpha}}{\partial Q_k} \right)_0 \right|^2, \quad (2.5)$$

where ν_0 is the incident light frequency. In the context of battery electrolytes, Raman spectroscopy is particularly valuable since it can detect symmetric vibrations invisible to FT-IR, making it highly effective for probing ion coordination, solvation

shell dynamics, and ion pairing, all of which are crucial for electrolyte design and performance optimization.

Complementing Raman spectroscopy, infrared absorption provides additional insights by probing variations of the molecular dipole moment during vibrations. Infrared spectroscopy detects vibrational transitions through absorption of IR radiation, which requires that:

$$\left(\frac{\partial\mu}{\partial Q_k}\right)_0 \neq 0, \quad (2.6)$$

where μ is the molecular dipole moment. The measured absorbance A follows the Beer–Lambert law:

$$A = \log_{10}\left(\frac{I_0}{I}\right) = \varepsilon cl, \quad (2.7)$$

where I_0 and I are the incident and transmitted intensities, ε is the molar absorptivity, c the concentration, and l the path length. The absorption intensity for vibrational mode k depends on the square of the dipole derivative:

$$I_k \propto N\tilde{\nu}_k \left|\left(\frac{\partial\mu}{\partial Q_k}\right)_0\right|^2, \quad (2.8)$$

with N being the molecular density and $\tilde{\nu}_k$ the vibrational frequency of mode k .

FT-IR spectroscopy is highly sensitive to polar functional groups and asymmetric vibrations, making it invaluable for monitoring ion pairing, solvation structures, and electrolyte decomposition in batteries.

Taken together, Raman and FT-IR spectroscopies are complementary tools for probing molecular vibrations. Their combined application enables a comprehensive molecular-level understanding of solvation, ionic interactions, and stability in battery electrolytes, thereby guiding the rational design of next-generation energy storage systems.

2.5 Gas Chromatography-Mass Spectrometry (GC-MS) for LP30 Electrolyte Analysis in LiFePO₄ Cells

Gas chromatography–mass spectrometry (GC-MS) combines high-resolution chromatographic separation of volatile compounds with definitive mass spectral identification. In the case of LP30 electrolyte (1 M LiPF₆ in a 50:50 v/v mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC)), GC-MS is capable of distinguishing intact solvents from degradation products such as alkyl carbonates and organophosphates, even in the presence of trace moisture. Through flexible chromatographic protocols and strict anhydrous handling, GC-MS enables the elucidation of molecular pathways responsible for SEI/CEI formation, capacity fade, and impedance growth in LiFePO₄ cells [21, 92].

In GC analysis, a microliter-scale aliquot of electrolyte extract, obtained by immersing separator material in acetonitrile, is injected into a heated inlet, vaporized, and carried by Helium through a capillary column. The stationary phase, such as cyanopropyl-modified polysiloxane, is chosen to resolve both low-boiling solvents and higher-boiling degradation products without derivatization. A typical temperature program begins with an isothermal hold at 40 °C to separate water (retention time

4–6 min) and methanol (5 min), followed by a ramp at 5 °C/min to 180 °C to elute DMC (6–8 min) and EC (10 min), and finally a faster ramp (10 °C/min) to 250 °C to release monoalkyl phosphates and carbonate oligomers. Ramp rates, hold times, and final temperatures can be tuned to adapt the method to different column dimensions or resolution requirements.

Eluted compounds are then introduced into an electron-impact ion source at 70 eV, generating characteristic fragment ions. A quadrupole mass analyzer separates these ions by mass-to-charge ratio through the application of radiofrequency and direct-current fields, transmitting only ions of the selected m/z . Full-scan acquisition (m/z 10–300) yields a spectrum for each chromatographic peak, which can be matched against reference libraries (e.g., NIST) to confirm compound identities.

Electrolyte extraction requires rigorous anhydrous handling. Fully discharged cells (2.5 V vs. Li/Li⁺) must be opened in an argon glovebox (O₂, H₂O < 1 ppm). Separator fragments and residual electrolyte on electrodes are transferred into acetonitrile, dissolving LiPF₆, EC:DMC, and volatile byproducts in a single step. Residual water, if present, appears as an early GC peak, clearly resolved from DMC and methanol. Maintaining < 100 ppm H₂O prior to injection is crucial to ensure that detected triflorophosphate (TFP) and organophosphate fragments reflect actual in-cell hydrolysis rather than artifacts introduced during handling.

Fresh LP30 extracts yield chromatograms with peaks corresponding to water (if present), DMC (m/z 74), and EC (m/z 88). Usually the EC:DMC peak area ratio is consistent with the nominal 50:50 mass ratio. Storage at 25 °C in sealed vials produces negligible spectral changes over several weeks, indicating minimal LiPF₆ decomposition under these conditions. In contrast, electrochemical cycling significantly alters the volatile profile, introducing new degradation signals.

In summary, GC-MS, when applied with stringent moisture control and adaptable temperature programs, provides a detailed molecular portrait of electrolyte evolution in LiFePO₄ cells. By quantifying intact EC:DMC, monitoring LiPF₆ hydrolysis and oxidative byproducts, and detecting minor volatile organic compounds, GC-MS elucidates the degradation pathways underlying SEI/CEI formation, capacity loss, and impedance rise. This makes GC-MS a fundamental tool for post-mortem electrolyte analysis, enabling both the identification of degradation products and the optimization of recycling processes as well as the formulation of next-generation electrolytes.

The methodological detail provided here is essential to ensure reproducibility and to establish a direct link between electrolyte degradation products and macroscopic cell performance, which will be further discussed in subsequent chapters.

Chapter 3

Structural Characterization of Calcium ion based electrolytes

Chapter Overview

This chapter focuses on the detailed characterization of the solvation structure of calcium ions in CaTFSI_2 /propylene carbonate electrolytes. The study employs polarizable molecular dynamics simulations enhanced by quantum mechanical calculations to refine the force field parameters, thereby providing a more accurate description of calcium coordination, complementing the insights obtained from classical fixed-charge models. Through a combination of radial distribution function analyses, coordination number calculations, and solvation shell composition studies, the work explores how calcium's local environment evolves with electrolyte concentration. Additionally, the simulation results are compared with experimental data from Raman spectroscopy to validate the computational models. This integrated approach enables a comprehensive understanding of calcium solvation behavior, highlighting the critical role of electronic polarization and offering insights into the ion-solvent and ion-anion interactions that shape the electrolyte structure. These results establish a robust framework for future investigations into electrolyte design for calcium-based energy storage applications.

3.1 Starting solubility tests

A rational starting point for the development of calcium battery electrolytes is the systematic evaluation of salt solubility in relevant solvents, as only those combinations that yield homogeneous, stable, and sufficiently concentrated solutions can enable meaningful electrochemical performance and reliable characterization. In this context, solubility tests were conducted for calcium tetrafluoroborate ($\text{Ca}(\text{BF}_4)_2$), calcium bis(trifluoromethanesulfonyl)imide ($\text{Ca}(\text{TFSI})_2$), calcium triflate ($\text{Ca}(\text{TfO})_2$), and calcium hexafluorophosphate ($\text{Ca}(\text{PF}_6)_2$) in four polar aprotic solvents: Propylene carbonate (PC), N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMA), and N,N-dimethylpropionamide (DMP). This approach is supported by recent literature, where salt-solvent compatibility is shown to be a prerequisite for advancing the chemistry of multivalent batteries [41, 43]. PC (Sigma-Aldrich, 310328), DMF

(TCI, D0793), DMA (TCI, D0641), and DMP (TCI, D0793) were used as received and further dried over activated molecular sieves as described below. The chemical structures of the investigated salts and solvents are reported in Figure 3.1.

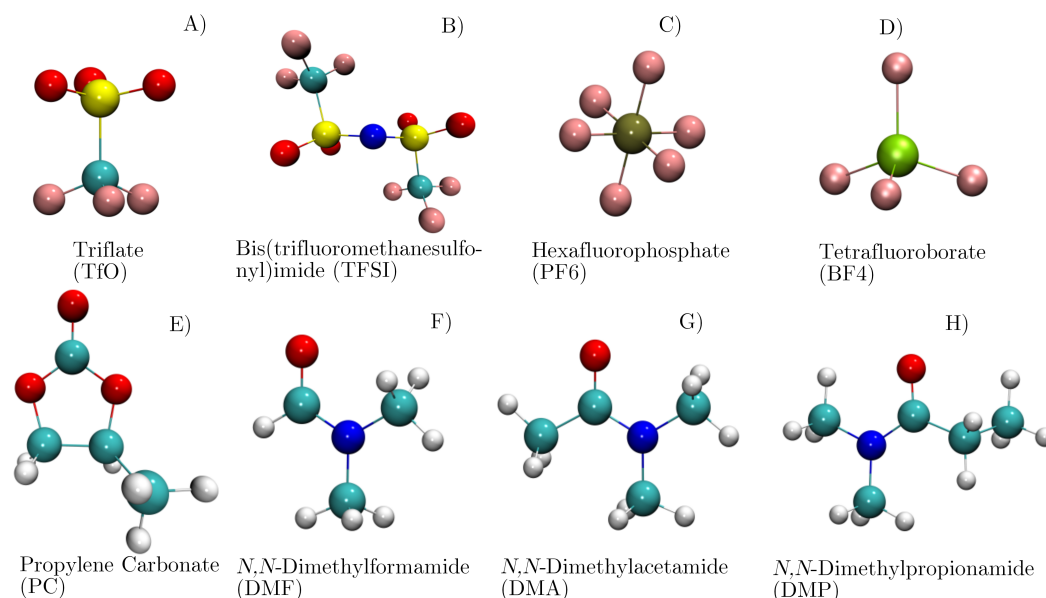


Figure 3.1 Chemical structures of the salts and solvents investigated in the solubility study: (a) triflate anion (TfO⁻), (b) bis(trifluoromethanesulfonyl)imide anion (TFSI⁻), (c) hexafluorophosphate anion (PF₆⁻), (d) tetrafluoroborate anion (BF₄⁻), (e) propylene carbonate (PC), (f) *N,N*-dimethylformamide (DMF), (g) *N,N*-dimethylacetamide (DMA), and (h) *N,N*-dimethylpropionamide (DMP).

The calcium salts Ca(TFSI)₂ (Sigma-Aldrich, 753122), Ca(TfO)₂ (Sigma-Aldrich, 515892), Ca(PF₆)₂ (Apollo Scientific, AP0H11A9CB34), and Ca(BF₄)₂ (Apollo Scientific, APO458955578) were dried prior to use by heating overnight in a Büchi at a temperature 100 °C. After this, the Büchi containing the salts was immediately transferred into the glovebox and opened only once under the glovebox atmosphere to minimize exposure to ambient moisture and oxygen (O₂ and H₂O < 1 ppm).

For the solubility tests, each solvent was transferred into an argon filled glovebox under controlled atmosphere conditions in order to minimize exposure to atmospheric moisture and oxygen. Inside the glovebox, to remove any residual water and oxygen, molecular sieves (type 3Å, 0.3 nm pore size, Sigma-Aldrich, 312345), previously activated by heating at 250 °C for 3 hours, were added to the solvents. The solvents were then left in contact with the sieves for a period of five days inside the glovebox, thus ensuring complete removal of dissolved moisture and oxygen. All operations, in the glovebox, were performed at room temperature (approximately 20–25 °C).

For each solvent thus treated, glass vials of 2 mL were prepared, each containing 1 mL of solvent. In contrast to the conventional procedure for solution preparation, in which the salt is weighed first and the solvent is subsequently added up to the desired volume, in this case the salt was incrementally added to a vial containing a fixed volume of solvent. This approach was chosen to optimize the use of materials, minimizing the amount of salt required for the experimental determination of the

solubility limit.

However, this method necessarily involves an approximation: with each addition of salt, the total volume of the solution increases slightly. In estimating the resulting concentration, it was assumed that such volume variation is negligible or at least constant over the course of the experiment. The salt aliquots were calculated to increase the nominal concentration by 0.1 M with each addition. After every addition, the solution was mixed using a vortex mixer to promote dissolution of the salt. The addition of salt was stopped upon the observation of a persistent precipitate, which was taken as an indication that the solubility limit of the system had been reached or exceeded.

The results of these systematic solubility tests are summarized in Table 3.1, which reports the observed solubility behavior of each calcium salt as a function of concentration and solvent. In this table, green and red color coding indicates, respectively, the presence or absence of complete salt dissolution at each concentration step. As shown, $\text{Ca}(\text{TFSI})_2$ and $\text{Ca}(\text{PF}_6)_2$ are soluble up to at least 1.0 M in all tested solvents, while $\text{Ca}(\text{TfO})_2$ displays limited solubility in amides solvents and is insoluble in PC. $\text{Ca}(\text{BF}_4)_2$ is essentially insoluble in all media. This visual summary further underscores the selection rationale described below.

While DMF, DMA, and DMP are effective at solvating these salts due to their strong

PF_6^- (mol/L)	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
DMF	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
DMA	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
DMP	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
PC	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
TfO^- (mol/L)	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
DMF	Y	Y	Y	Y	Y	Y	Y	N	N	N
DMA	Y	Y	Y	Y	Y	Y	Y	N	N	N
DMP	Y	Y	Y	Y	Y	Y	Y	N	N	N
PC	N	N	N	N	N	N	N	N	N	N
TFSI^- (mol/L)	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
DMF	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
DMA	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
DMP	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
PC	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
BF_4^- (mol/L)	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
DMF	N	N	N	N	N	N	N	N	N	N
DMA	N	N	N	N	N	N	N	N	N	N
DMP	N	N	N	N	N	N	N	N	N	N
PC	N	N	N	N	N	N	N	N	N	N

Table 3.1 Results of the solubility screening for $\text{Ca}(\text{BF}_4)_2$, $\text{Ca}(\text{TFSI})_2$, $\text{Ca}(\text{TfO})_2$, and $\text{Ca}(\text{PF}_6)_2$ in PC, DMF, DMA, and DMP at concentrations from 0.1 M to 1.0 M. Green cells indicate complete salt dissolution (soluble), while red cells indicate the presence of undissolved salt (insoluble) at the respective concentration. The yellow highlighted row marks the reference solution used for subsequent electrochemical characterization.

electron-donating ability and high dielectric constant, each presents significant drawbacks for practical calcium battery research. As detailed in recent studies, amide

solvents such as DMF possess relatively high donor numbers and can be chemically reactive at the calcium metal interface, increasing the risk of side reactions and surface passivation that limit reversible calcium cycling [93]. While DMA and DMP are structurally related, their specific reactivity at the calcium interface has not been systematically investigated to the same extent. DMP molecules, in particular, because of their size and shape, create more crowding around the dissolved calcium ions introducing additional steric hindrance. As a result, it becomes harder for the calcium ions to be efficiently solvated by solvent molecules. This can affect the salt's solubility, the structure of the solvation shell, and ultimately the ionic conductivity. PC, by contrast, offers several key advantages as a study solvent. While its viscosity is higher than that of amide solvents, PC's high dielectric constant and relatively weak donor properties promote efficient salt dissociation for both $\text{Ca}(\text{TFSI})_2$ and $\text{Ca}(\text{PF}_6)_2$. Moreover, these characteristics minimize strong solvent–cation interactions that can impede calcium plating and stripping [41].

The combination of high dielectric constant and limited coordinating ability makes PC an effective and reliable solvent for calcium battery electrolytes. Furthermore, PC is a standard in battery research due to its wide electrochemical stability window and its extensive use in battery studies. However, achieving interfacial stability toward calcium metal remains a challenge, even in PC-based electrolytes [43]. Electrochemical tests and structural studies have established that $\text{Ca}(\text{TFSI})_2$ in PC supports robust ionic conductivity in the 0.1–1.0 M range, with maximal conductivity observed near 0.5–0.6 M [41]. The bulky, charge-delocalized TFSI^- anion minimizes contact ion pairing and surface passivation, enabling reversible calcium deposition and dissolution with much greater efficiency than alternatives such as perchlorate or triflate salts [41, 43]. This behavior is reinforced by structural and volumetric analyses, which reveal that Ca^{2+} acts as a structure-making ion in O-donor solvents, forming highly coordinated solvation shells that further enhance salt dissociation and transport properties [93].

Therefore, based on the outcome of solubility screening, as well as the practical, electrochemical, and structural arguments drawn from recent studies, PC was chosen as the optimal solvent for detailed investigation of $\text{Ca}(\text{TFSI})_2$ electrolytes. This system maximizes the likelihood of achieving reversible calcium metal cycling, while minimizing confounding effects from solvent reactivity or limited salt dissolution. In addition, the use of PC as a solvent benefits from the extensive body of existing knowledge and characterization protocols developed for analogous lithium electrolytes, facilitating the interpretation and benchmarking of results for the calcium system. The concentration window of 0.1–1.0 M provides a reliable foundation for systematic study of calcium battery performance and enables comprehensive structural characterization of the electrolyte solutions, allowing correlation of electrochemical behavior with solvation structure and ion association phenomena.

3.2 Raman Spectroscopy and Analysis of the Electrolyte Structure

For the characterization of the reference solutions, consisting of $\text{Ca}(\text{TFSI})_2$ in propylene carbonate (PC) in the concentration range from 0.1 to 1.0 M, analysis was

performed by Raman spectroscopy. The solutions were prepared inside a glovebox, where both the salt and the solvent were handled as in the solubility tests. Specifically, a 1.0 M stock solution was prepared, subsequently, the more dilute solutions were obtained by taking the required volume of the stock solution with an Eppendorf pipette and adding pure solvent up to a final volume of 1 mL into a 1.0 mL quartz cuvette, which was subsequently closed and sealed with parafilm before being taken out of the glovebox. Once sealed, the Raman spectrum was acquired. The same cuvette was used for all solutions, and it was thoroughly washed with an excess of acetone and then placed in an oven, uncapped, at 60 °C for 20 minutes to ensure the absence of any residual solvent.

Raman spectra were acquired using a Raman spectrometer equipped with a 10x/0.25 objective to focus the sample and a He-Ne laser ($\lambda = 632.8$ nm). The instrumental parameters were as follows: 32 accumulations with an acquisition time of 60 seconds each; 1800 grooves/mm diffraction grating; 1000 μm entrance slit; 1150 μm confocal hole. These parameters were chosen to optimize spectral resolution and signal-to-noise ratio.

The collected spectra were then baseline-corrected using a custom Python script designed for interactive and flexible background removal. In this process, characteristic background points were manually selected from each spectrum interactively allowed precise point marking along the signal. These selected points were then used to fit a smooth baseline curve by interpolating with a third-order polynomial spline, chosen for its ability to capture the slow-varying background typical of Raman spectra. The interpolated baseline was subtracted from the original signal to isolate the Raman features of interest. The resulting baseline-corrected and normalized spectra for all concentrations are shown in Figure 3.2 and serve as the basis for the spectral analysis discussed below.

3.3 Assignment and Interpretation of Raman Vibrational Bands of Ca(TFSI₂) in PC Electrolytes

The vibrational Raman spectrum of the calcium electrolyte based on propylene carbonate (PC) and bis(trifluoromethanesulfonyl)imide (TFSI) was interpreted through a detailed comparison with density functional theory (DFT) simulations performed on optimized molecular clusters. The computational spectra were obtained using the $\omega\text{B97X-D}$ functional combined with the Def2-TZVP basis set within Gaussian-16 [94]. Simulated Raman spectra of isolated PC, isolated TFSI, Ca-PC, and Ca-TFSI complexes (whose structural motifs are shown in Figure 3.3) were convoluted using Voigt line shapes with a half-width at half-maximum (HWHM) of 4 cm^{-1} and a 50:50 Gaussian-Lorentzian ratio to mimic experimental broadening. These spectra were then linearly combined and compared directly to the experimental Raman spectrum of the 0.1 M Ca(TFSI₂) in PC electrolyte, as shown in Figure 3.3. The analysis reveals a good band-by-band correspondence between simulated and experimental spectra, which enables confident assignments of vibrational modes. A scaling factor of 0.98 along frequencies, for simulated spectras, was applied to correct for systematic overestimations inherent to the harmonic approximation.

In the low-frequency region (130–300 cm^{-1}), the simulated TFSI and Ca-TFSI

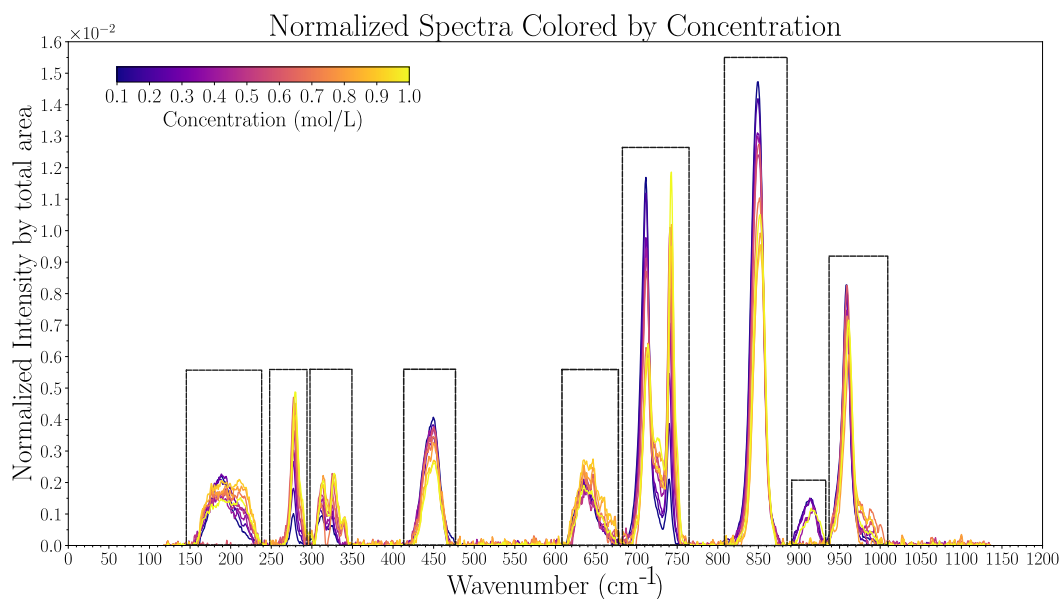


Figure 3.2 Baseline-corrected and normalized Raman spectra of $\text{Ca}(\text{TFSI})_2$ in propylene carbonate (PC) at varying concentrations (0.1–1.0 M). Black squares highlight the key vibrational regions analyzed and assigned to specific molecular modes of PC and TFSI, based on DFT simulations and literature benchmarks. These regions represent diagnostic features for solvation structure, ion pairing, and coordination effects.

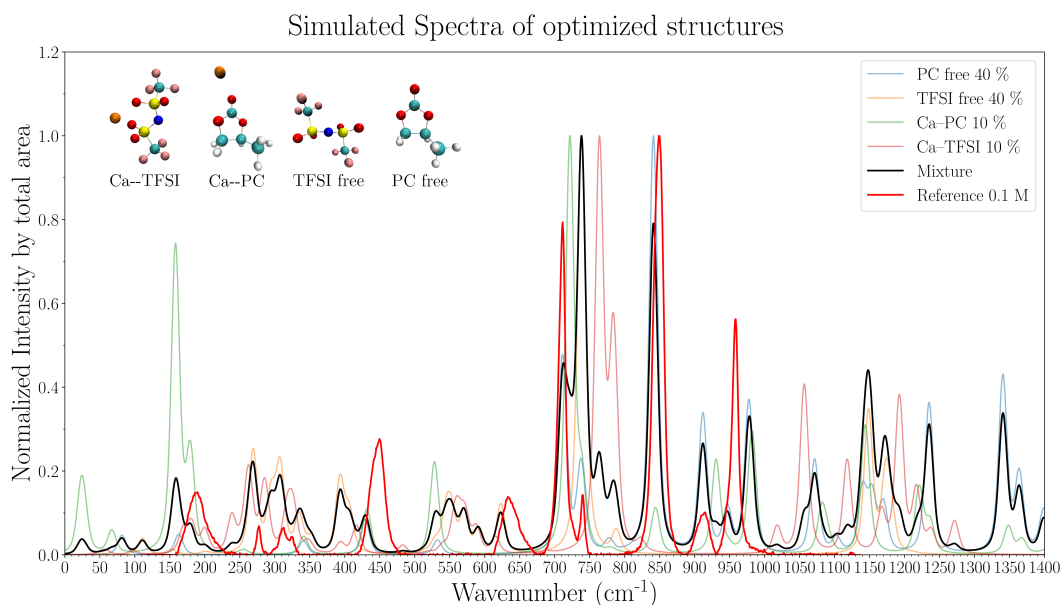


Figure 3.3 Normalized Raman spectra from DFT-optimized structures of PC free, TFSI free, Ca-PC, and Ca-TFSI complexes. Spectra are convoluted with Voigt profiles (4 cm^{-1} HWHM, 50:50 Gaussian-Lorentzian). The black trace represents the normalized linear combination (Mixture) which satisfactorily reproduces the experimental Raman spectrum of 0.1 M $\text{Ca}(\text{TFSI})_2$ in PC electrolyte.

clusters exhibit torsional and skeletal vibrational modes near 155, 180, and 280 cm⁻¹. These correspond well to experimental bands observed at approximately 160, 200, and 275 cm⁻¹, respectively. Notably, the Ca-induced deformation mode near 180 cm⁻¹ in the simulations matches an experimental shoulder at 200 cm⁻¹, confirming the influence of calcium coordination on the anion vibrational dynamics.

Between 300 and 450 cm⁻¹, the PC skeletal deformation mode at 347 cm⁻¹ is reflected in a weak experimental peak at 310–340 cm⁻¹. Additionally, overlapping PC ring bending and TFSI S–N–S angle deformation modes between 415 and 435 cm⁻¹ in the simulated spectrum correspond to experimental bands that form the peak at 420–480 cm⁻¹, highlighting the interplay between solvent and anion structural perturbations.

The 600–680 cm⁻¹ region is dominated by TFSI vibrational modes assigned to SO₂ wagging and S–C stretching, simulated at 610 and 630 cm⁻¹ and observed experimentally in the peak at 610–670 cm⁻¹. These shifts are consistent with the calcium coordination effects.

The fingerprint region between 680 and 780 cm⁻¹ exhibits good agreement: the PC ring breathing vibration at 712 cm⁻¹ in simulations matches the experimental peak at 715 cm⁻¹, while the TFSI SO₂–N–SO₂ backbone breathing mode simulated at 743 cm⁻¹ aligns with an experimental band near 745 cm⁻¹. This confirms the ability of the computational model in capturing coordination-specific vibrational signatures. In the 800–880 cm⁻¹ range, simulated the ring CH₂–CH₂ stretching modes appear at 825 and 860 cm⁻¹, matching experimental bands at 830 and 860 cm⁻¹. The subtle shoulders and band broadening seen in both spectra indicate complex vibrational coupling and heterogeneity in the solvation environment.

Finally, the high-frequency region between 930 and 1000 cm⁻¹ features strong PC carbonyl (C=O) stretching and O–CH₂ wagging modes. The simulated bands at 950 and 980 cm⁻¹ correspond to experimental peaks at similar frequencies, with slight red-shifts reflecting Ca²⁺ coordination-induced weakening of the C=O bond.

Overall, the consistent correspondence between simulated and experimental Raman spectra with a 0.98 factor for frequency shifting validates the DFT cluster approach and provides reliable band assignments related to ion pairing and solvation structure in Ca(TFSI₂)/PC electrolytes.

The analysis reveals a good band-by-band correspondence between simulated and experimental spectra, enabling confident vibrational mode assignments related to ion pairing. A complete summary is reported in Table 3.2.

3.4 Spectral Analysis of the Raman Fingerprint Region (680–780 cm⁻¹)

This section presents the systematic deconvolution of the 680–780 cm⁻¹ region. By resolving its composite bands and examining their evolution with concentration and coordination state, we probe the solvation environment and ion-pairing mechanisms governing the electrolyte system.

To decompose the band spanning 680–780 cm⁻¹, four Voigt functions were employed, each corresponding to one of the distinct vibrational features identified within this range: the PC ring breathing mode, the Ca²⁺-coordinated PC ring breathing, the

Experimental (cm^{-1})	Simulated (cm^{-1})	Assignment
160	155	TFSI torsional/skeletal modes
200	180	Ca-induced deformation in TFSI
275	280	TFSI skeletal modes
310–340	347	PC skeletal deformation
420–480	415–435	PC ring bending + TFSI S–N–S deformation
610–670	610–630	TFSI SO_2 wagging + TFSI S–C stretching
715	712	PC ring breathing
745	743	TFSI SO_2 –N– SO_2 backbone breathing
830	825	CH_2 – CH_2 stretching
860	860	CH_2 – CH_2 stretching
950	950	PC C=O stretching
980	980	PC OCH_2 wagging

Table 3.2 Summary table of experimental and simulated Raman bands with corresponding vibrational assignments for $\text{Ca}(\text{TFSI})_2$ in PC electrolyte.

TFSI symmetric breathing vibration, and the Ca^{2+} -coordinated TFSI breathing. These features represent structurally and electronically distinct environments that emerge with increasing ionic concentration and coordination complexity.

Each component was modeled using a Voigt line shape to faithfully capture both Gaussian broadening (instrumental and thermal effects) and Lorentzian contributions (intrinsic vibrational lifetimes). The Voigt profiles used in the deconvolution maintained a Gaussian contribution of approximately 60% and a Lorentzian contribution of 40%, calibrated based on instrumental characteristics. The fitting procedure was executed using a custom Python-based routine, which treats the spectrum as a linear combination of Voigt profiles. The algorithm optimizes the amplitude, center frequency, Gaussian width, and Lorentzian width for each peak using a non-linear least squares approach, with initial conditions either estimated heuristically or imported from pre-defined parameter files.

Prior to fitting, the spectra were area-normalized to ensure consistent comparison across samples and conditions. Parameter bounds were imposed to reflect physically reasonable values and to prevent numerical overfitting. The use of Voigt profiles, as opposed to purely Gaussian or Lorentzian functions, allows for an accurate reconstruction of the experimental envelope while maintaining interpretability in terms of molecular interactions.

Isolating and tracking the evolution of these four components provides quantitative insight into the concentration-dependent speciation of the electrolyte. The progressive emergence and shifting of the Ca-coordinated bands serve as direct indicators of contact ion pair (CIP) formation and higher-order aggregation. As reported in Figure 3.4, this approach provides a powerful, structure-resolved view of solvation dynamics in complex electrolyte systems and validates the vibrational assignments derived from DFT simulations and prior experimental studies [41].

The results from Voigt deconvolution, supported by the analysis data, provide a consistent and detailed picture of how the vibrational components evolve with concentration. At the lowest concentration (0.1–0.3 M), the Raman response in the

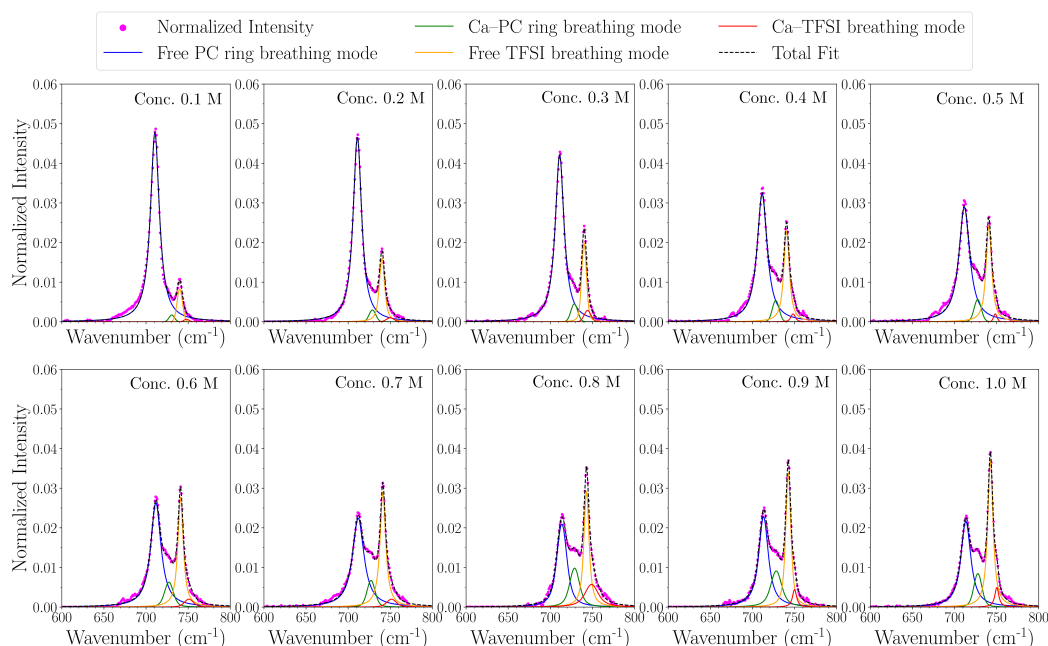


Figure 3.4 Experimental Raman spectra in the 680–780 cm^{-1} region for varying concentrations of $\text{Ca}(\text{TFSI})_2$ in PC, fitted using a sum of four Voigt functions. The individual peak components correspond to the PC ring breathing, Ca–PC ring breathing, TFSI breathing, and Ca–TFSI breathing modes. The evolution of peak position and intensity reflects changes in coordination environment and ion association as the salt concentration increases.

680–780 cm^{-1} region is dominated by two bands: one centered near 710–711 cm^{-1} , attributed to the ring breathing mode of free PC, and a broader, less intense feature at 743–744 cm^{-1} , corresponding to uncoordinated TFSI. The two coordination-induced bands, assigned to Ca^{2+} –PC and Ca^{2+} –TFSI breathing modes, are barely distinguishable at this stage.

As concentration increases to 0.4–0.6 M, the coordinated species begin to emerge more clearly. The Ca–PC breathing mode appears as a shoulder near 728–730 cm^{-1} , gradually gaining intensity, while the Ca–TFSI component becomes more evident around 748–749 cm^{-1} , suggesting the formation of contact ion pairs (CIPs). These spectral shifts are accompanied by a subtle blue shift of the free PC band (up to 713 cm^{-1}) and a red shift of the TFSI breathing (742 cm^{-1}), indicating progressive perturbation of both species due to cation coordination.

At the highest concentrations (0.7–1.0 M), the Ca-bound modes are prominent in the region. The Ca–PC breathing mode becomes more intense peaking around 729–730 cm^{-1} , while the Ca–TFSI band intensifies and shifts down to 745–746 cm^{-1} . This shift, along with the band broadening, reflects increased structural disorder and stronger electrostatic coupling within ion aggregates. The free PC band is still present, though with reduced intensity, reflecting the depletion of uncoordinated solvent molecules, which nevertheless remain one of the most abundant species in the system. Similarly, the intensity of the unbound TFSI mode reaches a plateau, suggesting that most anions are now involved in ion pairs or larger aggregates.

These findings confirm that the deconvoluted components effectively trace the evolving coordination structure of the electrolyte. Their distinct frequency shifts and intensity patterns support a concentration-driven transition from predominantly solvent-separated ion pairs to CIPs and eventually aggregated species. This evolution aligns well with both DFT predictions and literature on analogous Li^+ and Ca^{2+} electrolytes, emphasizing the robustness of Raman deconvolution as a probe of solvation structure in complex systems.

To complement this interpretation, Figure 3.5 shows the concentration dependence of key spectral metrics derived from Voigt deconvolution: (left) the relative area fractions of the Ca–PC and Ca–TFSI bands, (center) the peak position shifts of each component, and (right) the normalized area contributions of all species. Notably, at 0.5 M, the Ca–PC coordination reaches its maximum, while the Ca–TFSI band reaches its minimum, which corresponds to the conductivity maximum reported for this system [41].

The normalized area trends in the right panel reveal that the fraction of calcium coordinated by TFSI surpasses that coordinated by PC only at 0.9 M and 1.0 M. This shift implies a transition in solvation preference, with anion coordination becoming dominant at higher concentrations. Interestingly, the band shifts remain relatively stable across all concentrations, suggesting that the local geometry of the calcium coordination shell is not highly sensitive to salt concentration. This consistency supports the idea that calcium tends to form relatively stable complexes, likely involving one or two TFSI anions, with short-lived configurations that still permit full solubility across the examined concentration range. To further substantiate

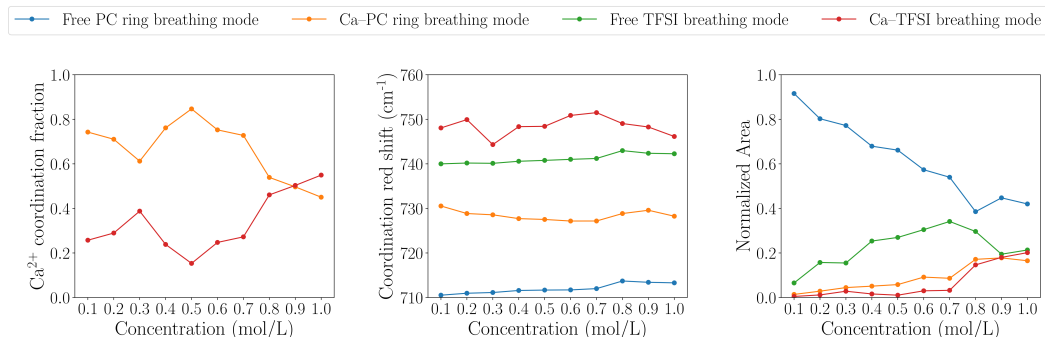


Figure 3.5 Left: Relative area fractions of Ca–PC and Ca–TFSI bands from Voigt deconvolution. Center: Vibrational band shifts versus concentration. Right: Normalized band areas of all four vibrational components. Together, these plots illustrate the evolution of coordination structure with salt concentration, highlighting the crossover in solvation dominance from PC to TFSI.

the vibrational deconvolution, the evolution of the Voigt line shape parameters, specifically the Gaussian width (σ), Lorentzian width (γ), and their ratio (γ/σ), was analyzed across the full concentration range. These parameters provide valuable insight into the mechanisms of spectral broadening and their correlation to underlying molecular interactions and dynamics.

As shown in Figure 3.6, the Gaussian width (σ), primarily reflecting inhomogeneous broadening, due to instrumental resolution and thermal disorder, exhibits relatively

moderate and non-monotonic variation with concentration across all bands. This suggests that local static disorder and thermal environments evolve only slightly with ionic strength. According to Figure 3.6, the Gaussian width (σ) exhibits varying trends depending on the vibrational mode. The Ca-PC band shows minimal variation across the concentration range, with changes remaining within 1.5 cm^{-1} , suggesting a relatively stable solvation geometry for this coordination environment. In contrast, more noticeable fluctuations in σ are observed for the free PC and both TFSI-related bands, indicating increasing local heterogeneity and static disorder as salt concentration rises. These differences reflect how coordination affects the rigidity and spatial variability of the solvation structures.

In contrast, the Lorentzian width (γ), associated with vibrational lifetime broadening and fast dynamic interactions, reveals more distinct patterns. Notably, the free PC band displays the highest γ values, reaching up to 8.15 cm^{-1} , particularly at intermediate concentrations, suggesting strong homogeneous broadening. This may indicate transient interactions or fast-exchanging coordination environments even for nominally unbound species. The Ca-TFSI band also exhibits substantial γ values, peaking at 7.03 cm^{-1} , consistent with a dynamically labile and electrostatically perturbed coordination shell. Meanwhile, the Ca-PC and free TFSI bands show more limited Lorentzian broadening with maxima of 3.84 and 3.99 cm^{-1} respectively, suggesting either greater structural rigidity or less frequent dynamic exchange.

The γ/σ ratio provides a composite view of the dominant broadening regime. Free PC consistently shows the highest γ/σ values except for 0.9 M concentration, exceeding 1.5 in several cases. This highlights its substantial homogeneous character, likely driven by rapid exchange between coordinated and free states. The Ca-TFSI band, while also exhibiting one elevated γ/σ ratio, does not dominate this metric as initially presumed, remaining below 1.4 across all concentrations. Both Ca-PC and free TFSI maintain low γ/σ values, generally below 1.1 , indicating predominantly inhomogeneous broadening and spectrally stable environments.

Taken together, the Voigt parameter analysis reinforces the spectral interpretation obtained from band intensities and positions. It highlights that even uncoordinated solvent molecules like PC can experience strong homogeneous broadening, possibly due to dynamic exchange with coordination sites or fluctuations in the solvation structure. These findings complement the observed trends in vibrational shifts and relative band areas, offering a more nuanced view of the interplay between dynamic solvation and ion pairing across concentration. They also underscore the mechanistic shift from static solvation to dynamically broadened coordination structures at high salt loadings, consistent with the transition from solvent-separated ion pairs to labile contact ion pairs and aggregates.

3.5 Classical Molecular Dynamics Simulations of Electrolyte Behavior

While the Raman spectroscopic analysis provided detailed insights into the vibrational characteristics and coordination environments of Ca^{2+} in PC-based electrolytes, it offers a predominantly static and ensemble-averaged view of the molecular structure. To complement and extend these findings, molecular dynamics (MD) simulations

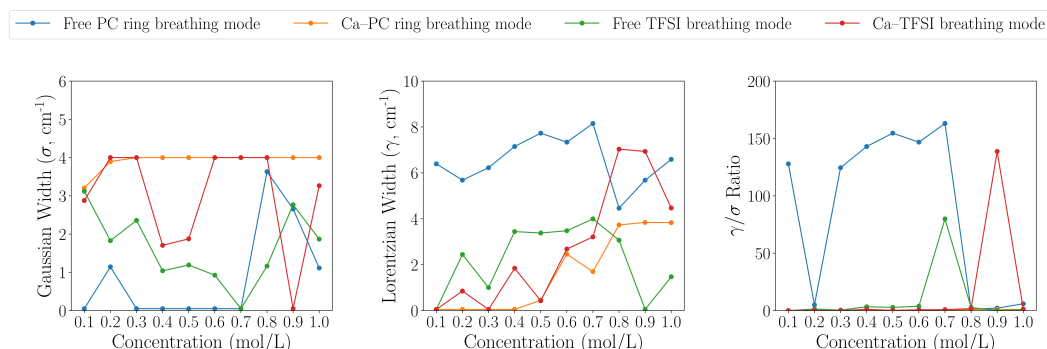


Figure 3.6 Gaussian width (σ , cm^{-1}), Lorentzian width (γ , cm^{-1}), and γ/σ ratio extracted from Voigt fitting of the $680\text{--}780\text{ cm}^{-1}$ region, plotted against $\text{Ca}(\text{TFSI})_2$ concentration in PC. The increasing γ and γ/σ for the coordinated species highlight enhanced vibrational damping and dynamic broadening with concentration, especially for Ca-TFSI.

were conducted to probe the time-resolved structural behavior of the electrolyte system at the atomistic level. Specifically, MD allows for the elucidation of local coordination geometries that are challenging to capture experimentally. These simulations serve to validate and interpret the experimental observations, while also providing insight into the mechanisms of solvation, and coordination as a function of salt concentration. In this section, we detail the simulation methodology, parameterization strategies, and analysis protocols, followed by a critical comparison of the MD results with the Raman spectral trends reported in the previous sections. To establish a validated molecular dynamics protocol and identify the appropriate calcium parameters to use, classical MD simulations were first carried out on a 0.1 M solution of Ca^{2+} in SPC/E water. The simulation system consisted of 3 Ca^{2+} ions and 1663 SPC/E water molecules, arranged within a cubic simulation box with a side length of $36.83\text{ \AA}$ and a positional tolerance of $2.5\text{ \AA}$, using Packmol software [95]. This aqueous reference system served to benchmark the accuracy of structural observables such as the ion–oxygen distance (IOD) and coordination number (CN) against experimental data. The Ca^{2+} ion was modeled using the PME-compatible Lennard-Jones parameters reported by Li and Merz [75], optimized to reproduce hydration structure under Ewald summation conditions in explicit SPC/E water. The parameters used were $\varepsilon = 0.40953\text{ kJ/mol}$ and $\sigma = 2.91\text{ \AA}$, consistent with Particle Mesh Ewald (PME) electrostatics and the SPC/E model. Simulations were performed using LAMMPS [96] with a timestep of 1 fs and full periodic boundary conditions. Electrostatic interactions were treated using the PPPM solver with a relative accuracy of 10^{-5} , and van der Waals interactions were truncated at $12.0\text{ \AA}$. Constraints on O–H bond lengths and H–O–H angles in water were enforced using the SHAKE algorithm. The simulation protocol consisted of three main stages:

1. NPT Equilibration and Density Calibration: following energy minimization (steepest descent and conjugate gradient with energy and force tolerances of 10^{-7} and 10^{-9} , respectively), the system was equilibrated in the NPT ensemble for 12 ns at 300 K and 1 atm. Temperature and pressure were maintained using a Nosé–Hoover thermostat and an isotropic Nosé–Hoover barostat, ensuring

canonical sampling of the NPT ensemble under isotropic pressure control. To eliminate transient effects, the average density was computed using only the final 10 ns of the trajectory. The simulation cell was then isotropically rescaled to match this equilibrium density, ensuring a physically realistic starting configuration for further simulations.

2. Annealing Procedure: to overcome metastable trapping and promote efficient exploration of the configurational space, a temperature-annealing protocol was performed over a total of 10 ns. The procedure consisted of five identical annealing cycles, each comprising:
 - A linear heating ramp from 300 K to 600 K in 10 increments of 30 K, with 100 ps of NVT dynamics at each temperature (1.0 ns total);
 - A linear cooling descent from 600 K to 300 K in 10 decrease of 30 K, with 100 ps of NVT dynamics at each temperature (1.0 ns total);

Each increment used a Nosé–Hoover thermostat with a damping parameter of 100 fs. The full annealing sequence spanned 5 cycles $\times$ 2.0 ns = 10.0 ns, enhancing solvation shell reorganization and ion-solvent sampling.

3. NVT Production Run: after annealing, the system was returned to 300 K and propagated under NVT conditions for 50 ns, using a Nosé–Hoover thermostat with the same damping factor used before. Atomic coordinates and thermodynamic data were sampled every 1 ps for trajectory analysis. Restart files were written regularly for fault tolerance.

This multistage protocol ensured thorough equilibration of the system, yielding a density and hydration structure in close agreement with experimental observations. It provided a statistically robust ensemble for the evaluation of structural descriptors such as radial distribution functions, coordination numbers, and solvation dynamics, thereby establishing a rigorous foundation for extending the methodology to more complex carbonate-based electrolyte systems in subsequent simulations.

To validate the structure of the calcium hydration shell, the radial distribution function (RDF) between calcium ions and water oxygen atoms was computed from the production trajectory. The resulting profiles for both RDF and the coordination number $CN(r)$ are reported in Figure 3.7. The RDF exhibits a sharp primary peak centered at approximately 2.45 Å, indicative of a well-defined first solvation shell with strong ionic coordination. Integration of $CN(r)$ up to a cutoff radius of 3.00 Å yields a coordination number of 7.7. Both the Ca–O distance and coordination number are in excellent agreement with experimental values reported for aqueous Ca^{2+} [97, 98]. Beyond the first shell, a broader secondary peak in the RDF emerges between approximately 4.00 Å and 5.50 Å, corresponding to the second hydration layer. This second shell is less structured and more diffuse, as expected from weaker hydrogen-bond-mediated interactions and dynamic water exchange. The coordination number increases gradually in this region, reflecting the onset of longer-range solvation effects that contribute to the overall stabilization of the ion in solution.

After validating the simulation protocol on the aqueous solution and establishing the calcium parameters to be employed, the same methodology was applied to a

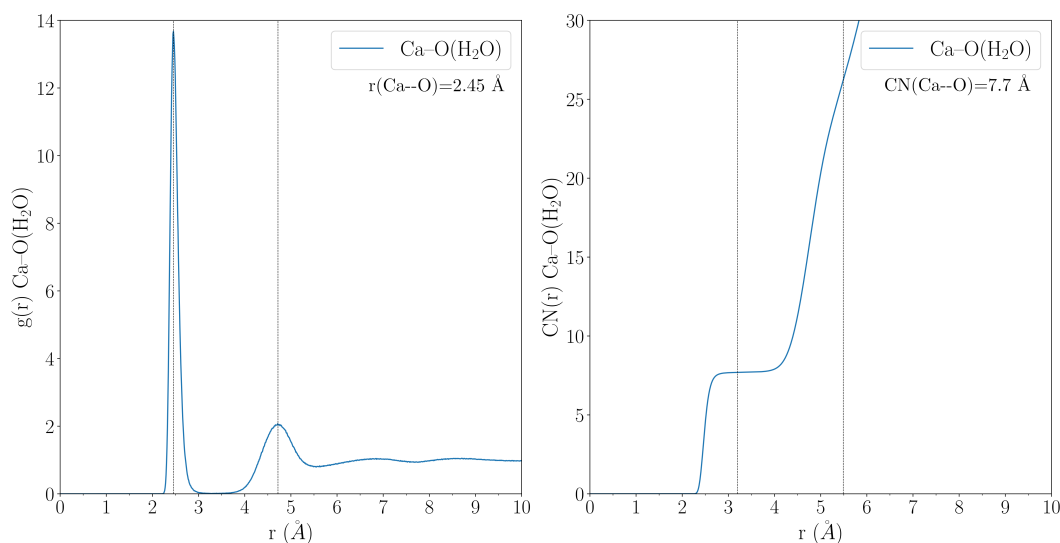


Figure 3.7 Radial distribution function $g(r)$ (left) and coordination number $\text{CN}(r)$ (right) for $\text{Ca-O(H}_2\text{O)}$ in 0.1 M aqueous Ca^{2+} solution. The sharp first peak approximately at 2.45 Å indicates strong hydration of Ca^{2+} ions. The coordination number plateaus at 7.7 within a cutoff of 3.00 Å , consistent with literature values for the first solvation shell of calcium in water. A broader second peak centered near 4.70 Å reflects the onset of the second hydration shell, characterized by weaker and more transient ion-solvent interactions. Vertical dashed lines highlight the approximate boundaries of the first and second solvation shells.

0.1 M solution of calcium-bis(trifluoromethanesulfonyl)imide Ca(TFSI)_2 in propylene carbonate (PC). The simulation cell was composed of 3 Ca^{2+} ions, 6 TFSI anions, and 347 PC molecules, corresponding to a nominal salt concentration of 0.1 M. The initial configuration was prepared using Packmol [95], following the same procedure described previously. Molecules were placed within a cubic simulation box with a side length of 36.95 Å , enforcing a minimum interatomic distance of 2.5 Å to prevent steric clashes. This configuration yields a density consistent with the experimental value for pure PC at ambient conditions, namely 1.198 g/cm^3 [99]. The density estimated after the first NPT equilibration stage of the 0.1 M $\text{Ca(TFSI)}_2/\text{PC}$ system was 1.21 g/cm^3 . The parameters used for calcium were the same as those employed in the SPC/E water model. For the TFSI anion, parameters were adopted from the OPLS-AA force field optimized for ionic liquids [69], while for propylene carbonate (PC), parameters were taken from the OPLS-AA force field for organic molecules [68]. The simulation protocol used for this system was identical to that described for the aqueous case: energy minimization, NPT equilibration with density calibration, cyclic thermal annealing, and a final NVT production run. This approach ensures methodological consistency and allows for a direct comparison between the hydration structure in water and the solvation behavior in organic media.

To characterize the solvation environment of Ca^{2+} in propylene carbonate at 0.1 M concentration, RDFs and $\text{CN}(r)$ were computed for Ca-O(PC) and Ca-O(TFSI) pairs. The results are reported in Figure 3.8. The Ca-O(PC) RDF shows a sharp peak centered at 2.47 Å , indicating strong coordination of the carbonate oxygen to

Ca^{2+} . Integration of the $\text{CN}(r)$ curve up to $3.52 \text{ \AA}$ yields a coordination number of 8.8, confirming that the carbonate solvent plays a dominant role in the primary solvation shell of calcium.

The Ca-O(TFSI) RDF features a smaller first peak centered at $2.55 \text{ \AA}$, with a corresponding coordination number of only 0.2 when integrated up to $3.45 \text{ \AA}$. This indicates that direct coordination of TFSI anions to Ca^{2+} is minor under dilute conditions, consistent with a solvent-separated ion pair regime. Another weak peak placed near $4.70\text{--}5.30 \text{ \AA}$ in the Ca-O(TFSI) profile marks the beginning of the second shell, likely reflecting transient electrostatic interactions with non-coordinating anions.

These results validate the coordination trends inferred from Raman spectroscopy and highlight the dominant role of PC in stabilizing Ca^{2+} through strong inner-shell interactions. They also reinforce the accuracy of the force field parameters and simulation methodology used, which reliably capture both local structure and long-range solvation characteristics in non-aqueous electrolytes. Given the intrinsic

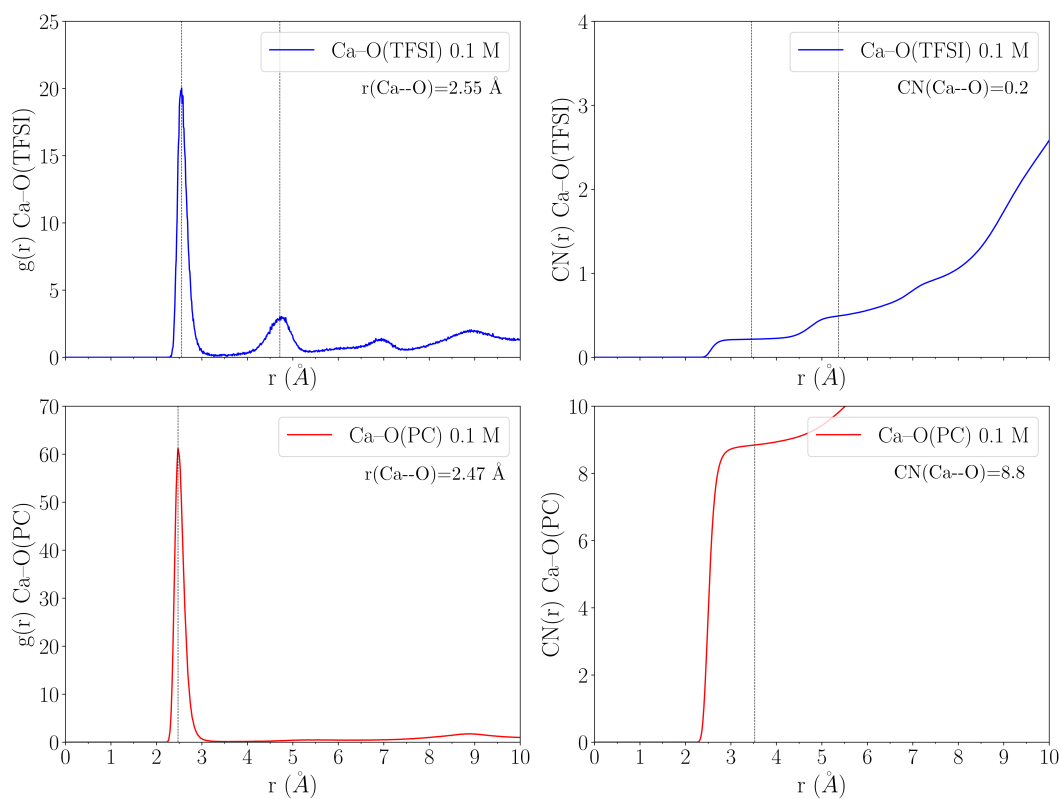


Figure 3.8 Radial distribution functions $g(r)$ and coordination numbers $\text{CN}(r)$ for Ca-O interactions in a $0.1 \text{ M Ca(TFSI)}_2/\text{PC}$ system. Top: Ca-O(TFSI) , Bottom: Ca-O(PC) . The first coordination shell is centered at $2.47 \text{ \AA}$ for PC ($\text{CN} = 8.8$) and $2.55 \text{ \AA}$ for TFSI ($\text{CN} = 0.2$). Vertical dashed lines denote the boundaries of the first and second solvation shells for each interaction.

limitations of classical molecular dynamics in describing electrostatics, particularly in systems involving multivalent ions, a correction scheme was applied to rescale the partial charges of ionic species based on quantum mechanical calculations. To

this end, a physically motivated charge-scaling procedure was adopted to compute a statistically representative scaling factor for the calcium ion.

First, a hybrid Bash-Tcl workflow running within the VMD [100] software, with Topotools [101] plugin, was developed to extract solvation clusters from the MD trajectory. The implemented workflow automatically identified calcium-centered clusters by selecting all atoms within the first solvation shell, as defined by RDF-based distance cutoff of 3.52 Å. To ensure chemical relevance and eliminate artifacts associated with periodic boundary conditions, only Ca^{2+} ions located at least one shell radius away from the box boundaries were considered. Furthermore, clusters were sampled every 250 ps, significantly longer than the estimated lifetime of a first solvation shell ≈ 20 ps, to guarantee statistical independence and avoid overcounting correlated configurations. The shell information, precomputed and encoded ensure that the extracted clusters were chemically consistent and physically representative of the dynamical solvation environment.

After the extraction process, 114 clusters were obtained. Each cluster was then subjected to a single-point DFT calculation using the $\omega\text{B97X-D}$ functional and the Def2-TZVP basis set, as implemented in the Gaussian-16 [94] and Multiwfn [102] software. Electrostatic potential (ESP) fitting was performed using the CHELPG scheme [103], which reconstructs atomic charges by reproducing the molecular ESP evaluated on a grid of points positioned outside the van der Waals surface of the molecule. The CHELPG method was selected over alternative population analysis schemes, including Mulliken [104], Hirshfeld [105], and Merz–Kollman [106], due to its balanced combination of physical accuracy, numerical robustness, and suitability for automation in large-scale workflows.

The Mulliken method, based on partitioning of basis function overlap populations, is known for its computational efficiency but suffers from strong sensitivity to basis set choice and often yields nonphysical charge distributions, particularly in systems with diffuse electron density. Hirshfeld analysis improves on this by using stockholder partitioning of the electron density, resulting in more stable charges, but tends to systematically underestimate charge separation and polarization effects. Merz–Kollman, which like CHELPG fits the ESP, places fitting points on Connolly surfaces and is highly dependent on molecular geometry and surface definition, making it less ideal for analyzing structurally diverse solvation clusters. In contrast, CHELPG charges offer a more transferable and physically relevant representation of atomic electrostatics, especially in systems dominated by intermolecular interactions. Its grid-based approach provides reproducible results with reduced sensitivity to molecular conformation, which is critical for batch processing of multiple solvation snapshots in the present study.

Grid points for ESP fitting were positioned on van der Waals radii sourced from a systematic dataset [107], which provides consistent and physically grounded parameters for all main group elements. This ensures that the electrostatic potential is sampled in chemically relevant regions while avoiding core artifacts, thereby enhancing the accuracy and stability of the charge-fitting process.

The computed charges on calcium from each cluster were normalized to the formal +2 charge, and the resulting values were compiled into a histogram, illustrating the distribution of effective scaling factors, as reported in Figure 3.9. The distribution exhibits a clear maximum at 0.86, which was adopted as the effective scaling factor.

This factor was then uniformly applied to the nominal charges of the Ca^{2+} and TFSI atoms in the force field for subsequent classical MD simulations. This methodology ensures improved electrostatic realism while maintaining compatibility with the fixed-charge MD framework.

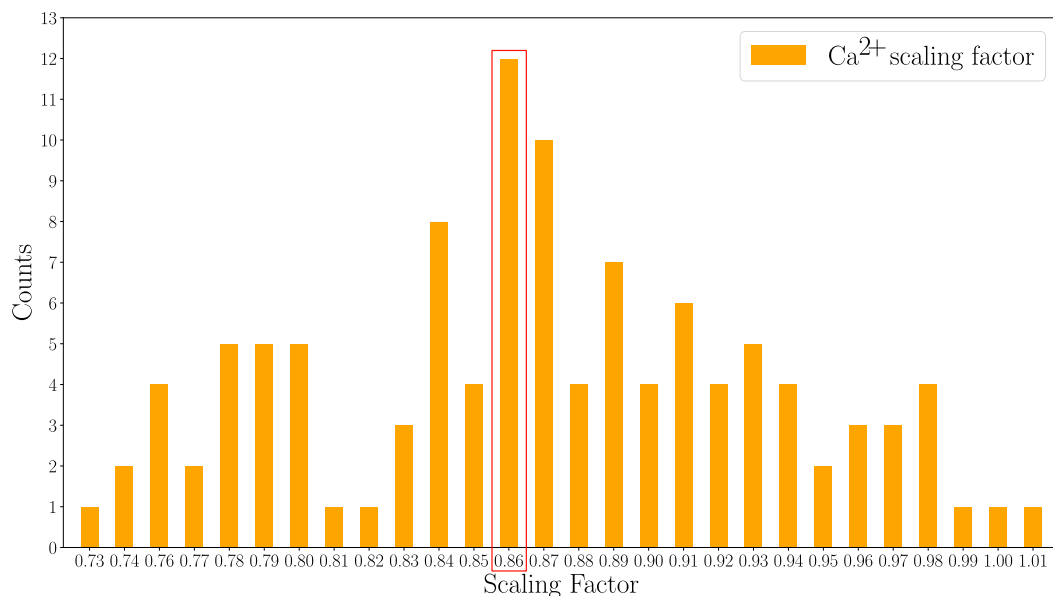


Figure 3.9 Histogram of computed charge scaling factors derived from CHELPG analysis of first-shell Ca^{2+} solvation clusters. The most probable value is 0.86, which was adopted as the effective scaling factor.

A new classical MD simulation of the $\text{Ca}(\text{TFSI})_2/\text{PC}$ system at 0.1 M concentration was then performed using the same rigorous protocol previously established. This methodological consistency ensures that any differences observed in structural properties can be unambiguously attributed to the use of scaled charges rather than variations in simulation conditions. The simulation box for the scaled-charge simulation was constructed using the density value estimated from the initial unscaled-charge NPT simulation, ensuring consistent system density between both simulations.

To assess the impact of charge scaling on the solvation structure, RDFs and coordination CNs were computed for $\text{Ca-O}(\text{TFSI})$ and $\text{Ca-O}(\text{PC})$ pairs, and compared with the reference unscaled simulation. The resulting profiles are reported in Figure 3.10. The RDF comparison reveals that applying the 0.86 scaling factor leads to a systematic modulation of the calcium coordination environment. For the $\text{Ca-O}(\text{TFSI})$ interaction, the position of the first solvation peak shifts slightly from 2.55 Å (unscaled) to 2.60 Å (scaled), reflecting a modest relaxation of the cation–anion interaction. Notably, the coordination number at the first minimum decreases from 0.2 (unscaled) to 0.0 (scaled), indicating a slight reduction in TFSI coordination upon charge scaling.

In contrast, the $\text{Ca-O}(\text{PC})$ interaction shows a first peak shift from 2.47 Å (unscaled) to 2.52 Å (scaled), again indicating a softening of the ion–dipole interaction. However, the coordination number here increases, rising from 8.8 (unscaled) to 8.9

(scaled), suggesting that the scaled electrostatics facilitate PC access to the first coordination shell.

These observations demonstrate that charge scaling leads to a more realistic solvation structure reducing overcoordination and unphysical binding of solvent molecules, a known artifact in fixed-charge force fields. Moreover, the RDF profiles show that while the first solvation shell is directly affected by scaling, the second shell remains qualitatively similar, with broad features indicating diffuse solvent organization. At this point, it was possible to proceed with the simulation of solutions at other

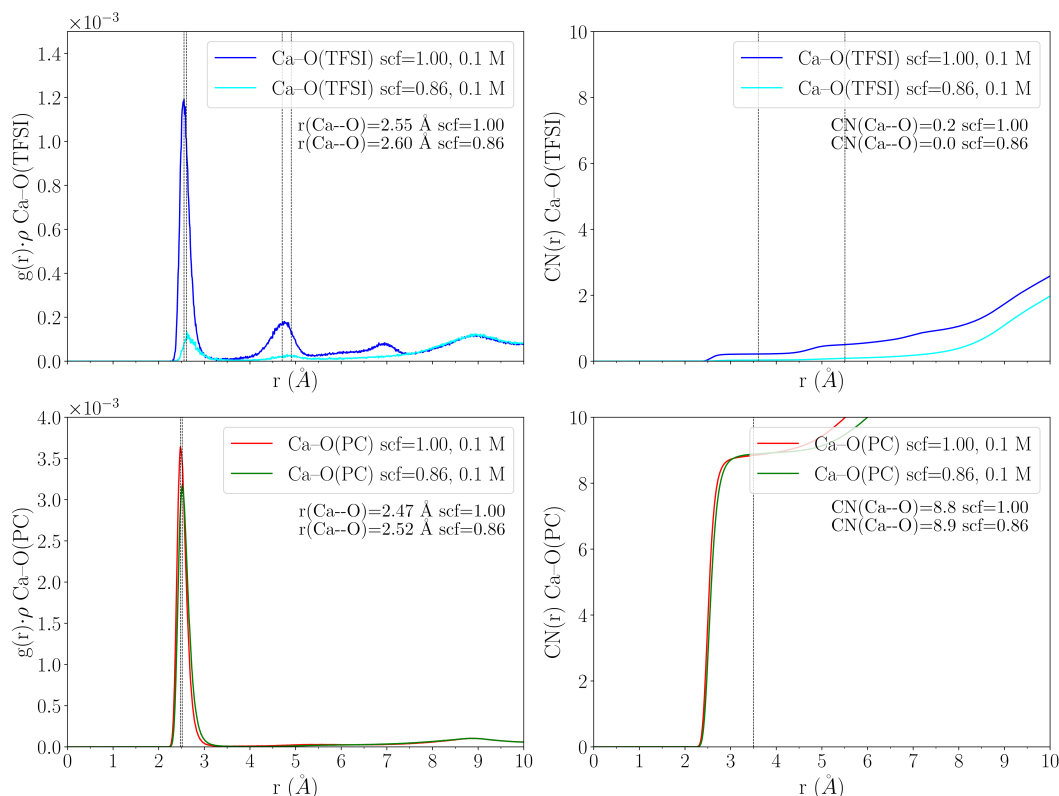


Figure 3.10 Comparison of radial distribution functions $g(r)$ multiplied by the species number density ρ , and coordination numbers $CN(r)$ for Ca-O(TFSI) and Ca-O(PC) at 0.1 M concentration, computed using full charges ($scf = 1.00$) and scaled charges ($scf = 0.86$). Top: RDF and CN for Ca-O(TFSI); Bottom: RDF and CN for Ca-O(PC). Charge scaling results in a slight shift and broadening of the first peak, and a modest increase in PC coordination.

concentrations, maintaining the charge scaling factor constant. The simulation protocol remained the same as previously described. The different simulation boxes were created using the same method, where the density for the initial configuration was taken from the density estimated for the system at the immediately lower concentration (for example, the box for 0.2 M was created using the density estimated for the 0.1 M solution, the 0.3 M box used the density from the 0.2 M solution, and so forth).

Once the simulations were completed, the estimated density was compared with the experimental density reported in Figure 3.11, and the radial distribution functions

(RDFs) were calculated following the same procedure as previously described. The resulting RDFs, shown in Figure 3.12, reveal interesting trends with increasing electrolyte concentration. The first solvation shell around the Ca^{2+} ions, characterized

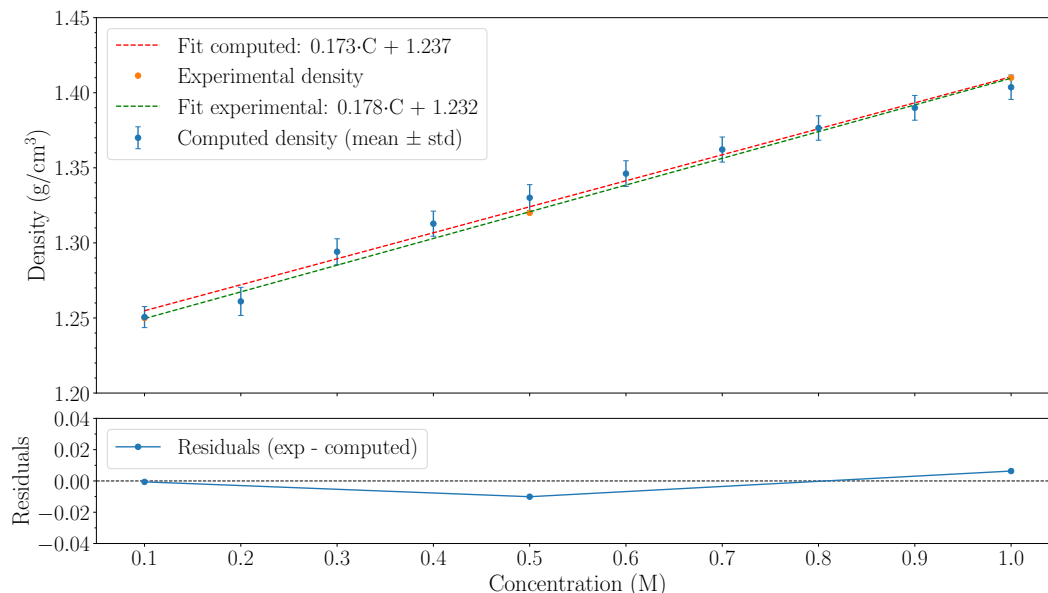


Figure 3.11 Comparison between computed and experimental densities across different concentrations. The computed density points represent the mean values with error bars indicating the standard deviation. Linear fits to both computed and experimental data are shown as dashed lines. The bottom panel displays residuals between experimental and computed densities.

by the sharp peak in the Ca-O(TFSI) and Ca-O(PC) RDFs, remains well defined across all concentrations, indicating stable and strong ion-solvent coordination. However, as the concentration increases, the first peak broadens slightly and its height diminishes, suggesting increased structural disorder and more competition for coordination sites due to the higher ion density.

Additionally, the second solvation shell, reflected in the broader features beyond the first peak (typically between 4 and 6 Å), exhibits less pronounced changes, remaining relatively diffuse and consistent in shape. This indicates that the overall solvent organization beyond the immediate coordination sphere is less sensitive to concentration changes, maintaining a somewhat fluid-like, dynamic structure.

The coordination numbers, obtained by integrating the RDFs up to the first minimum, show a modest decrease in PC coordination with increasing concentration, confirming that solvent molecules slightly reduce their presence around the calcium ion. Meanwhile, coordination with TFSI oxygen atoms shows a modest increase, consistent with the strong but less flexible binding nature of the anion and its increased presence in the first solvation shell.

Overall, the RDF analysis indicates that the charge scaling approach tends to produce more realistic solvation structures at higher concentrations, capturing subtle variations in ion-solvent interactions while mitigating artifacts such as overcoordination. To extend the analysis across the full concentration range, the computed coordination numbers were plotted as a function of Ca(TFSI)_2 concentration, span-

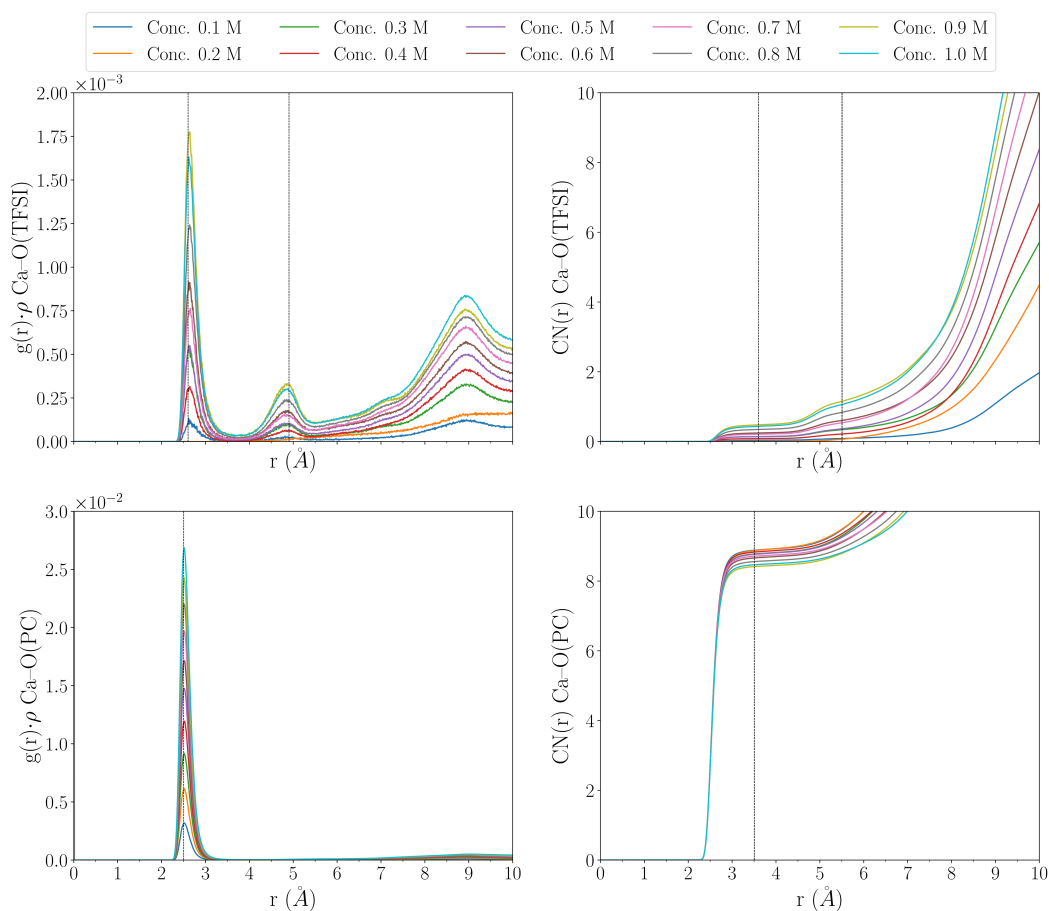


Figure 3.12 Radial distribution functions $g(r)$ multiplied by the number density of the observed species ρ , for Ca–O(TFSI) and Ca–O(PC) pairs at varying electrolyte concentrations from 0.1 M to 1.0 M. The first solvation shell remains well defined, with the main peak broadening and decreasing in height as concentration increases, indicating more structural disorder and competition for coordination sites. The second shell shows less variation, consistent with diffuse solvent organization. Coordination numbers ($CN(r)$), obtained from integration of the RDFs, suggest a modest increase in PC coordination at higher concentrations, while TFSI coordination remains nearly constant.

ning from 0.1 M to 1.0 M. The resulting trends are reported in Figure 3.13. The data show that the coordination number between calcium and the oxygen atoms of TFSI increases with salt concentration, rising from 0.0 at 0.1 M to 0.4 at 1.0 M. This trend reflects the progressive replacement of solvent molecules by coordinating anions as the ionic strength of the system increases, leading to a more compact and anion-rich solvation shell.

Conversely, the Ca–O(PC) coordination number decreases slightly, from 8.90 at 0.1 M to 8.50 at 1.0 M, suggesting a modest displacement of PC molecules from the first shell as TFSI coordination increases. At the highest concentrations, nearly all Ca^{2+} ions are coordinated by TFSI anions, consistent with the formation of contact ion pairs and higher-order aggregates observed in Raman spectroscopy.

These coordination number trends confirm the concentration-driven evolution of the calcium coordination environment, highlighting a transition from solvent-dominated to more anion-rich solvation as salt concentration increases and supports the spectroscopic findings.

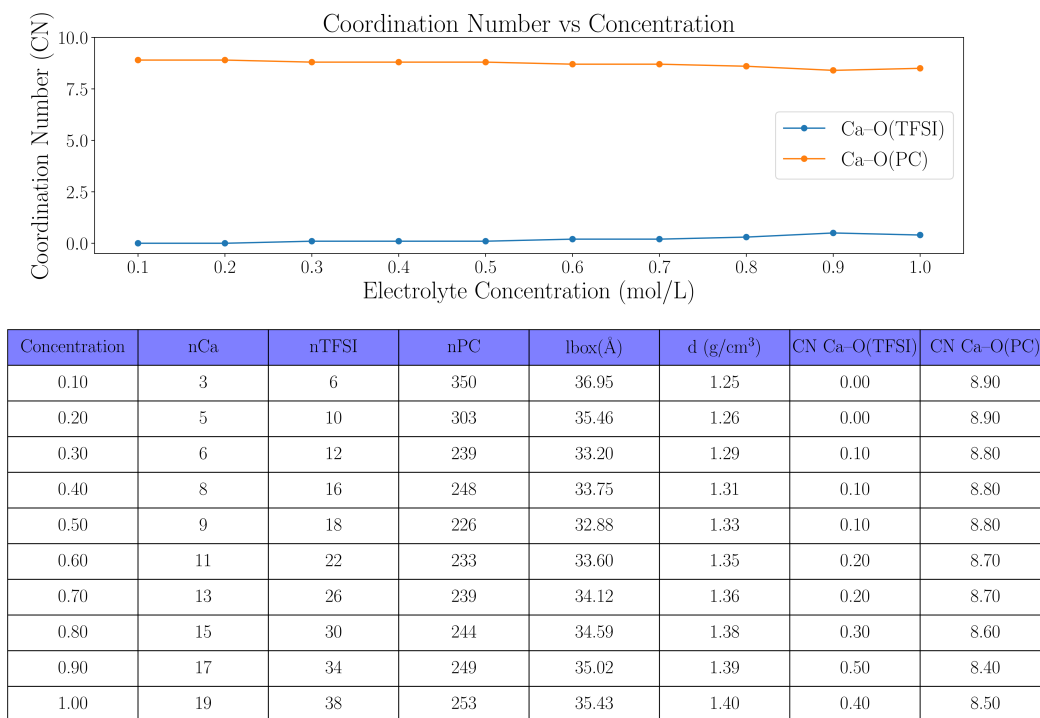


Figure 3.13 Coordination numbers of Ca^{2+} with TFSI and PC oxygen atoms as a function of electrolyte concentration. Values are extracted from MD simulations at each concentration using cutoff distances of 3.60 Å for Ca–O(TFSI) and 3.50 Å for Ca–O(PC), corresponding to the first minimum in their respective radial distribution functions. The data reveal a progressive increase in TFSI coordination with salt concentration, while the coordination environment remains predominantly PC-dominated.

3.6 DFT Calculations and Solvation Effects

To bridge the gap between classical molecular dynamics simulations and the experimentally obtained Raman spectra, density functional theory (DFT) calculations were carried out on a representative set of solvation clusters extracted from the MD trajectory at 0.1 M concentration. Three distinct calcium coordination environments were identified based on the first-shell configurations sampled during the simulation. These were selected to reflect the key solvation motifs observed: (a) a more anion-rich configuration with 1 Ca^{2+} , 2 TFSI^- , and 7 PC, (b) a mixed coordination state with 1 Ca^{2+} , 1 TFSI^- , and 8 PC, and (c) a fully solvent-separated state with 1 Ca^{2+} and 9 PC molecules, as shown in the top panel (a–c) of Figure 3.14. These clusters were extracted from well-equilibrated frames, selected to avoid proximity to the box edges and sampled every 250 ps to ensure statistically independent solvation environments. Geometry optimizations were performed using the ORCA 5.0.0 [108] software at

the ω B97X-D3/Def2-TZVP level of theory with the RIJCOSX approximation and Def2/J auxiliary basis set. As illustrated in the lower panels (d–f) of Figure 3.14, the optimized clusters exhibit changes in coordination relative to their MD-extracted precursors. Notably, the initially nine-fold Ca–PC cluster and the one-TFSI, eight-PC cluster both relaxed to six-fold coordination. Likewise, the cluster containing two TFSI molecules converged to a structure featuring one TFSI and six PC molecules coordinating the calcium ion. In all cases, the average Ca–O coordination distance was approximately 2.40 Å. These results confirm that classical MD simulations slightly overestimate the number of coordinated PC molecules, while DFT-optimized structures reflect a tighter and more chemically reasonable coordination geometry.

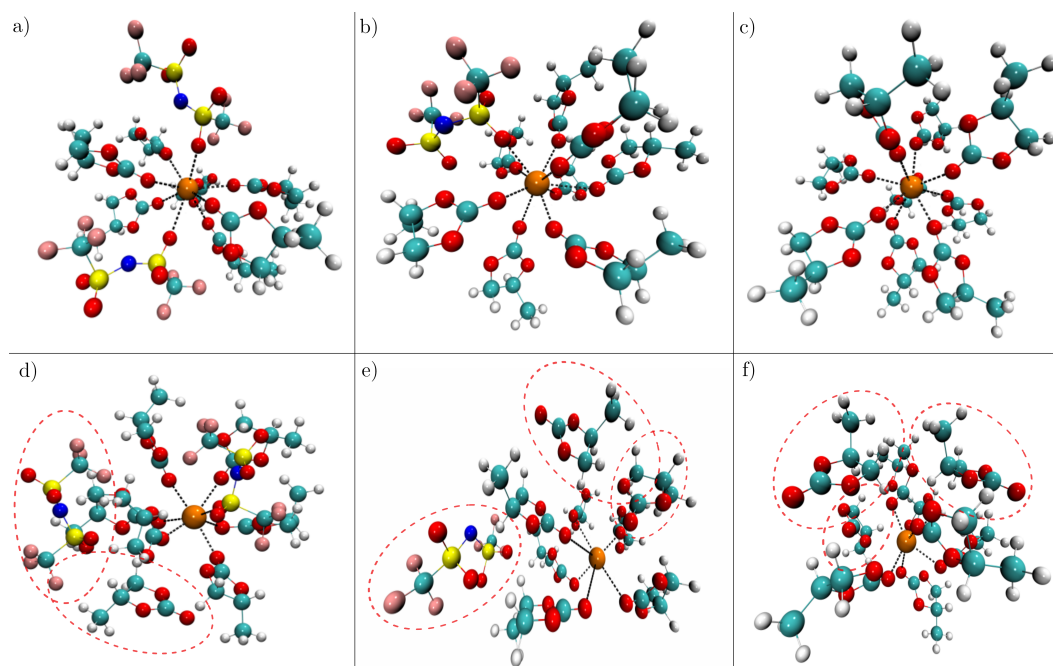


Figure 3.14 Extracted (a–c) and optimized (d–f) solvation clusters used for DFT-based vibrational simulations. Structures correspond to: (a,d) $\text{Ca}^{2+} + 2 \text{ TFSI} + 7 \text{ PC}$; (b,e) $\text{Ca}^{2+} + 1 \text{ TFSI} + 8 \text{ PC}$; (c,f) $\text{Ca}^{2+} + 9 \text{ PC}$. Optimization at the ω B97X-D3/(Def2-TZVP+Def2/J) level reveals relaxation to lower coordination environments, yielding (d) $\text{Ca}^{2+} + 1 \text{ TFSI} + 6 \text{ PC}$ and (e, f) $\text{Ca}^{2+} + 6 \text{ PC}$. Residues excluded from the solvation shell are highlighted with red circles. The optimized structures exhibit an average Ca–O coordination distance of approximately 2.40 Å.

Following geometry optimization, vibrational frequency calculations were performed using Gaussian-16 [94] on two clusters: the $\text{Ca}^{2+} + 1\text{TFSI} + 6\text{PC}$ structure and the unique optimized $\text{Ca}^{2+} + 6\text{PC}$ configuration derived from the two clusters that initially featured one TFSI within the first solvation shell and were otherwise coordinated only by PC. Raman activities were computed and converted into spectra using the same protocol employed for the interpretation of experimental Raman data, including scaling of 0.98 along frequencies and Voigt broadening to match instrumental resolution. The simulated spectra are shown in Figure 3.15, alongside the experimental spectrum of the 0.1 M solution for direct comparison. In the fingerprint region between 680–780 cm^{-1} (Figure 3.16), which provides a sensitive probe of ion pairing

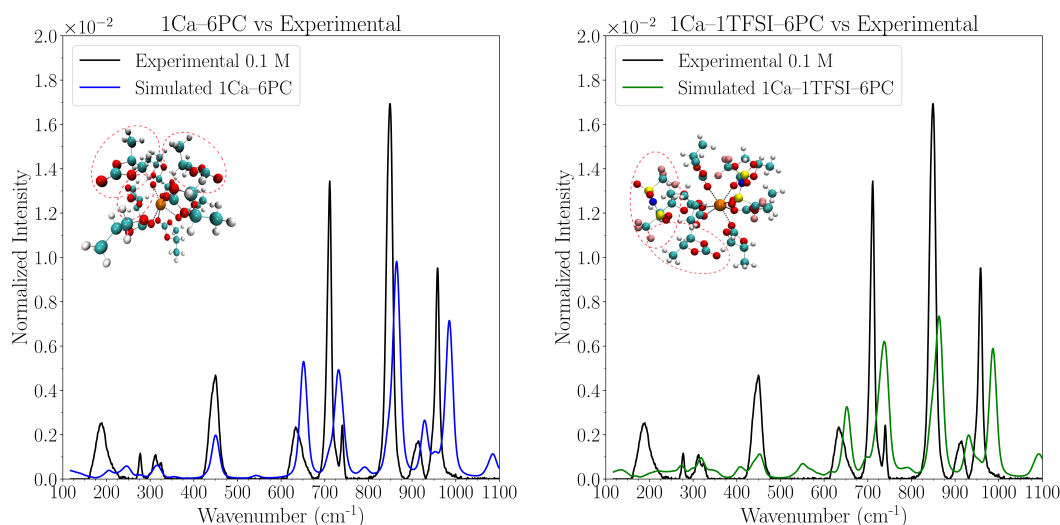


Figure 3.15 Simulated Raman spectra of DFT-optimized Ca^{2+} solvation clusters compared with experimental data at 0.1 M. Spectra were obtained from frequency calculations with Gaussian-16, scaled by a factor of 0.98, and processed using Voigt line-shape convolution to replicate experimental conditions. Residues excluded from the solvation shell are highlighted with red circles.

and solvent coordination, the comparison is particularly instructive. Experimental Voigt deconvolution (Figure 3.4) identified four components: a PC ring breathing mode at 710.5 cm^{-1} , a Ca-PC breathing feature at 730.5 cm^{-1} , a TFSI breathing mode at 740.0 cm^{-1} , and a Ca-TFSI vibration at 748.1 cm^{-1} .

The DFT spectrum of the $\text{Ca}^{2+}+6\text{PC}$ cluster (Figure 3.16, left) reproduces the PC ring breathing at $708\text{--}711\text{ cm}^{-1}$ and shows a distinct shift to $729\text{--}732\text{ cm}^{-1}$ upon coordination, consistent with the experimental Ca-PC feature. In the $\text{Ca}^{2+}+1\text{TFSI}+6\text{PC}$ cluster (Figure 3.16, right), the PC ring breathing mode shifts from $695\text{--}698\text{ cm}^{-1}$ to $729\text{--}732\text{ cm}^{-1}$, accompanied by the emergence of TFSI-related modes. The symmetric SO_2 deformation of TFSI is found at $738\text{--}741\text{ cm}^{-1}$, and a Ca-TFSI coupled vibration at $744\text{--}747\text{ cm}^{-1}$, both consistent with experimental assignments. These spectral features clearly demonstrate that the new bands arise from anion coordination and ion pairing.

Altogether, these DFT results demonstrate that the Raman spectral features observed experimentally originate from well-defined vibrational modes of specific solvation structures. Although the intensities are not well reproduced, since simulating only clusters cannot replicate bulk conditions, the spectral match in the fingerprint region underscores the chemical accuracy of the cluster models and the capacity of DFT to resolve the structural origin of vibrational markers. This integrated approach, combining classical MD sampling, DFT optimization, and vibrational spectroscopy, provides a valid framework for understanding solvation in calcium-based electrolytes.

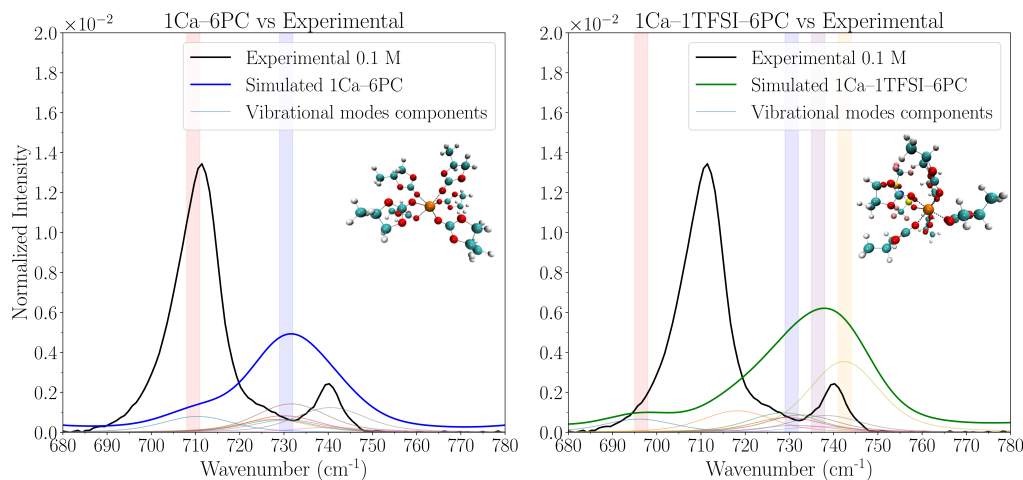


Figure 3.16 Experimental Raman spectrum (0.1 M, black) compared with DFT-simulated spectra, scaled by a factor of 0.98 and broadened using Voigt profiles (blue: 1Ca6PC cluster; green: 1Ca1TFSI6PC cluster) in the 680–780 cm^{-1} region. Colored bands highlight the PC breathing mode shift (red/blue) and the symmetric SO_2 stretching mode of TFSI (violet/orange). Individual vibrational contributions are shown as semi-transparent curves. The optimized solvation clusters employed for the DFT-based vibrational simulations are also displayed.

3.7 Polarizable Molecular Dynamics Simulations of Electrolyte Behavior

While classical molecular dynamics (MD) simulations and DFT calculations provided important insights into calcium solvation, a significant limitation persisted due to the systematic overestimation of coordination numbers arising from the fixed-charge approximation. To address this and introduce a more physically grounded electrostatic description, a polarizable force field approach was adopted using AMOEBA [77] within the Tinker-HP [82] software framework.

To determine the optimal parameters for calcium ions, as done before for classical molecular dynamics, we start by modeling the calcium–water system since experimental reference data are available for this case [97, 98]. The simulated system consisted of a single Ca^{2+} ion solvated by 553 water molecules, confined within a periodic cubic simulation cell with an edge length of 25.51 Å. The initial configuration was generated using the Packmol software [95], following the identical protocol applied in classical molecular dynamics simulations. This configuration corresponds to a concentration of 0.1 M. Importantly, the box size is smaller than that used in classical simulations, reflecting the higher computational cost associated with polarizable MD. As a result, the simulation protocol was accordingly adjusted.

Specifically, each system underwent a two-step equilibration in the NVT ensemble. Energy minimization was first performed using steepest descent with a convergence threshold of 10^{-5} Debye/atm on the dipole RMS to relax the system’s initial configuration. This was followed by a 100 ps NVT equilibration at 500 K to enhance

sampling and facilitate escape from potential local minima. After the 500 K simulation, the system was directly cooled to 300 K for a further 500 ps NVT run, allowing for structural relaxation and thermal equilibration at ambient temperature. Both stages used a velocity-Verlet integrator with a 1 fs timestep, temperature coupling via a Berendsen thermostat, and PME electrostatics with a real-space cutoff of 7.0 Å. Analytical long-range van der Waals corrections were also applied.

Two different parameterizations for calcium were tested: AMOEBA-2009 [109] and AMOEBA-2020 [110], which differ primarily in their Lennard-Jones (van der Waals) parameters while the Thole damping factor is the same. Four water models, AMOEBA-2003 [109], AMOEBA-2014 [109], AMOEBA-2020 [110], and AMOEBA-2022 [109], were paired with Ca^{2+} to evaluate the sensitivity of the solvation structure to force field choice. This led to the simulation of the following combinations: Ca(2009)/H₂O(2003), Ca(2009)/H₂O(2014), Ca(2009)/H₂O(2022), and Ca(2020)/H₂O(2020).

Radial distribution functions (RDFs) between calcium and the oxygen atoms of water were calculated from the equilibrated 300 K trajectories. The resulting profiles are shown in Figure 3.17, along with coordination numbers CN(r) computed up to the first minimum of each RDF. These were compared directly to experimental data for Ca^{2+} in water [97, 98]. Following the production simulations, the radial

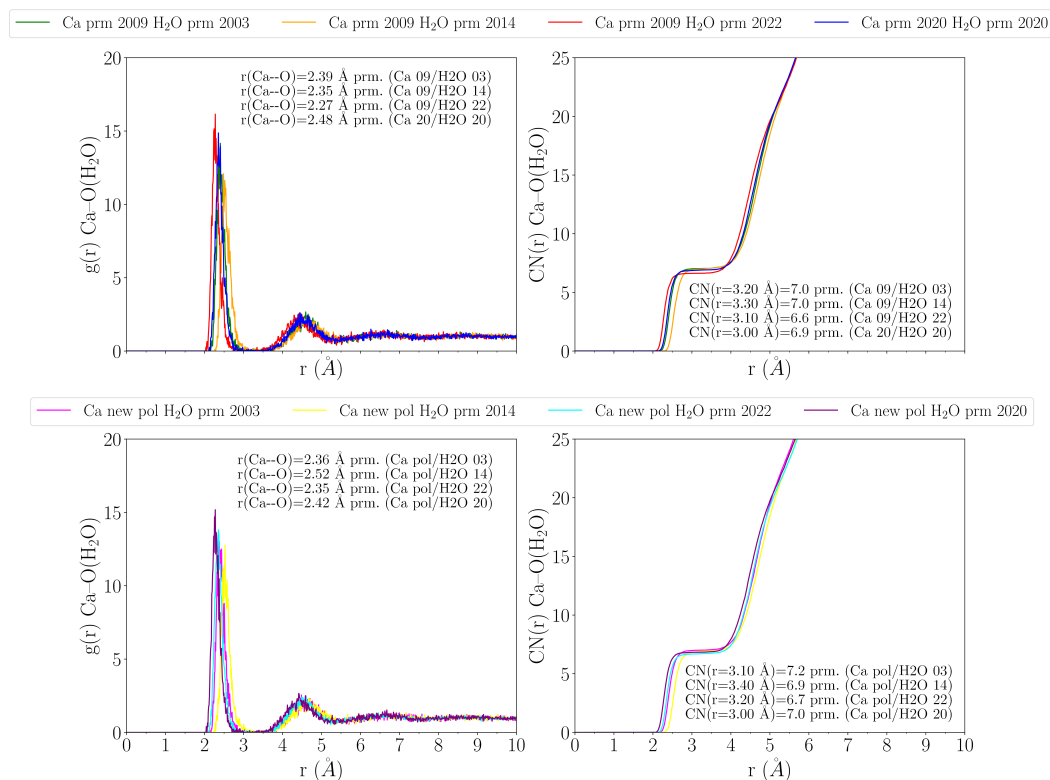


Figure 3.17 Radial distribution functions $g(r)$ between Ca^{2+} and water oxygen atoms obtained from polarizable MD simulations using different AMOEBA force field parameter sets. Top panel: results with the original force field combination; bottom panel: results with the refined DFT-based calcium polarization parameters. Coordination numbers (CN(r)) were calculated by integrating each $g(r)$ up to its first minimum.

distribution functions (RDFs) and integrated coordination numbers $CN(r)$ were analyzed to compare solvation characteristics across different parameterizations. All systems exhibit a pronounced first solvation peak located between 2.27 and 2.48 Å, reflecting the strong electrostatic attraction between Ca^{2+} and surrounding water oxygen atoms.

Integration of $CN(r)$ up to the first minimum of the RDF, ranging between 3.00 and 3.30 Å, reveals that the first-shell coordination number varies not so much, from 6.6 in the Ca-2009 + H₂O-2022 force field to 7.00 in Ca-2009 + H₂O-2003. These values are lower than those obtained from classical simulations, confirming the expected coordination number reduction when including polarization effects.

Second-shell coordination numbers, defined as the increment of $CN(r)$ between the first minimum and a cutoff of 5.55 Å, range between approximately 20.0 and 21.2. This indicates that even beyond the primary shell, calcium remains strongly solvated in a structured solvation environment, consistent with long-range electrostatic organization induced by the divalent ion.

Overall, the results underscore the importance of force field parameter selection in accurately reproducing solvation structure.

Among the models tested, the Ca(2020)/H₂O(2020) combination provided the most accurate structural descriptors, exhibiting a Ca–O peak distance of 2.48 Å and a coordination number of 6.9. While the coordination number is slightly lower than the experimental reference range of 7.6–8.1, the Ca–O distance falls within the reported literature values of 2.42–2.46 Å [97, 98]. Since the initial polarizable MD simulations did not fully reproduce the experimental coordination environment of Ca^{2+} in water, the polarizability of the calcium ion was computed using high-level electronic structure theory. Specifically, DLPNO-MP2 with DKH relativistic corrections and the cc-pwCVQZ-DK basis set was employed via ORCA 5.0.0 [108]. The calculated polarizability was then incorporated into the AMOEBA force field, generating new parameters.

With these updated parameters, simulations were repeated using the same protocol described earlier. The computed RDFs and corresponding coordination numbers $CN(r)$ for the various combinations of polarizable water and calcium models are presented in Figure 3.17. The first solvation shell is clearly defined by a sharp peak in RDF, centered between 2.36 and 2.52 Å, depending on the water model. Coordination numbers integrated up to the first minimum in the RDF, ranging from 3.00 to 3.40 Å, reveal first-shell coordination numbers between 6.7 and 7.2. Notably, the Ca-pol + H₂O-2003 model yields the highest first-shell coordination number, whereas the Ca-pol + H₂O-2020 model achieves a coordination number of 7.0 while maintaining the closest coordination distance to the experimental data. These values are similar but represent a clear improvement over the earlier models in terms of calcium polarization parameters.

The results from the RDF and CN analyses demonstrate that the new parameter sets, incorporating explicitly calculated polarizability of Ca^{2+} , more accurately reproduce its solvation environment in water. Particularly, AMOEBA-2020, when combined with these refined calcium parameters, yield significantly lower coordination numbers than classical fixed-charge models, aligning better with experimental data. This improvement underscores the critical role of polarization effects in defining the coordination shell and validates the simulation protocol employed. Subsequently,

the initial force field parameters for the bis(trifluoromethanesulfonyl)imide (TFSI) anion and propylene carbonate (PC) solvent were generated using the automated Poltype2 workflow [111].

This approach begins with geometry optimizations and electrostatic potential calculations performed at the ω B97X-D/6-311G** level of theory. Atomic multipoles were then derived by fitting the molecular electrostatic potential to distributed multipole expansions centered on atomic sites. Molecular polarizabilities were evaluated at the ω B97X-D/aug-cc-pVTZ level, providing explicit treatment of electronic polarization. Bonded and nonbonded parameters, including van der Waals terms, were assigned through database matching of atom types and empirical rules embedded in Poltype2. After this automated parameter generation, the force field parameters were refined to reproduce the calcium coordination environment obtained from DFT calculations of the extracted clusters from the CaTFSI₂ solution in PC at 0.1 M concentration. This refinement ensures that the force field accurately captures the ion–solvent and ion–anion interactions consistent with quantum mechanical references, thus enabling reliable molecular dynamics simulations of the electrolyte system.

After optimizing all force field parameters to accurately reproduce the coordination observed in DFT-optimized clusters, molecular dynamics simulations of CaTFSI₂ in PC solutions were performed across concentrations ranging from 0.1 to 1.0 M. These simulations adhered to the previously established protocol, featuring extended run times of 500 ps at 500 K and 4.5 ns at 300 K. For analysis, only the final 4 ns of the 4.5 ns simulation at 300 K were utilized.

From the equilibrated 300 K trajectories, RDFs between calcium ions and oxygen atoms of both TFSI anions and PC molecules were computed to characterize the calcium solvation structure as a function of concentration. The primary solvation shell exhibits a peak centered at 2.42 Å, with its boundaries identified at the first minima of the RDFs: 3.25 Å for Ca–O(TFSI) and 3.00 Å for Ca–O(PC). Analysis of the data in Figure 3.18 shows that the first solvation shell of calcium is well-defined and stable across the studied concentration range for both TFSI and PC oxygens. The peak positions in $g(r)$ remain consistent with increasing concentration, indicating a robust local solvation environment. However, the peak heights and coordination numbers exhibit concentration-dependent variations, reflecting subtle changes in ion pairing and solvent structuring.

Specifically, the coordination number of TFSI oxygen atoms bound to calcium increases with concentration, reaching approximately 3.4 at 1.0 M, while the coordination number of PC carbonyl oxygens decreases slightly from about 5.8 at 0.1 M to 2.2 at 1.0 M. The resulting trends are reported in Figure 3.19. These findings indicate a shift in calcium’s solvation environment from being more solvent-coordinated at low concentration to a greater anion contribution at higher concentrations, consistent with enhanced ion pairing. These results demonstrate the good ability of the developed polarizable force field and simulation protocol to capture the dynamic and structural features of calcium solvation in CaTFSI₂/PC electrolytes over a wide concentration range.

To provide a more accurate description of the calcium solvation shell, an analysis and classification procedure was implemented through a hybrid Bash-Tcl workflow executed in VMD [100] software. This approach allowed calculation of the percentage composition of calcium’s first solvation shell over the trajectory. The solvation shell

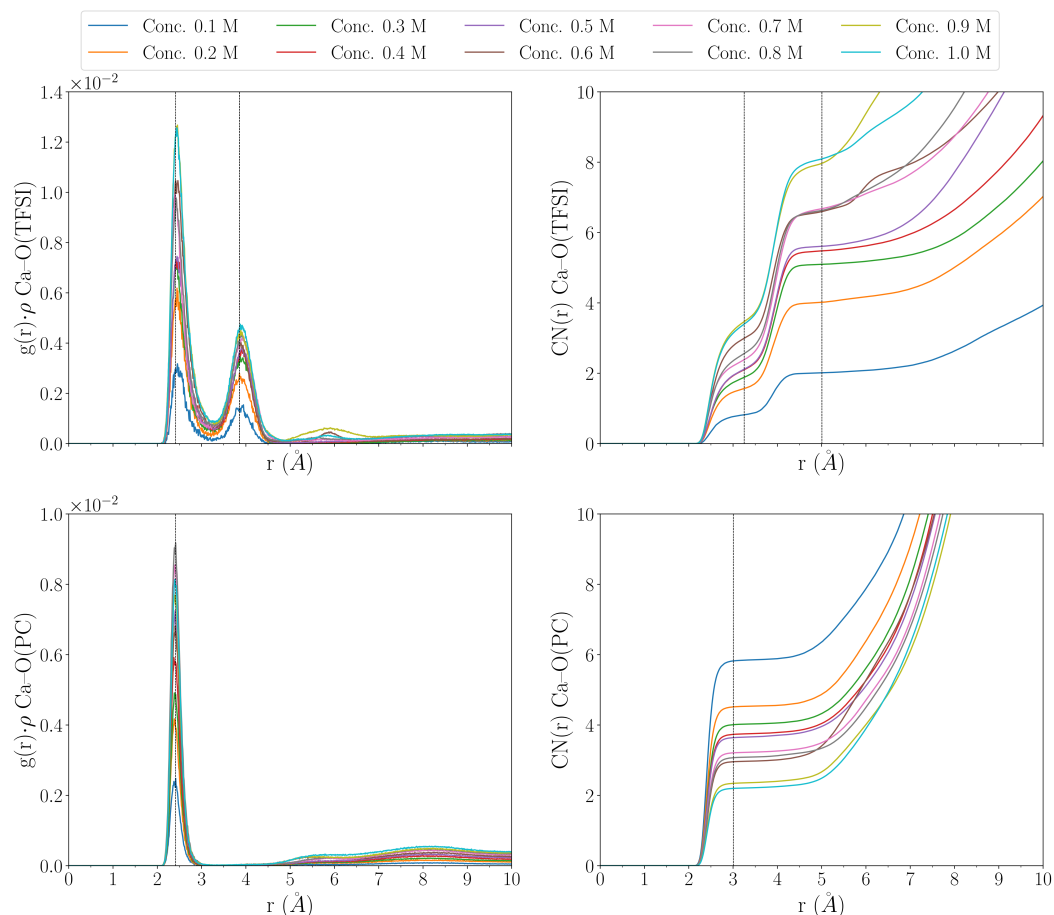


Figure 3.18 Radial distribution functions $g(r)$ multiplied by the number density of the observed species ρ and coordination numbers $CN(r)$ for Ca^{2+} -O interactions with TFSI (top row) and propylene carbonate (PC) (bottom row) oxygen atoms in $\text{CaTFSI}_2/\text{PC}$ electrolytes at various concentrations. Left panels show RDFs for concentrations from 0.1 to 1.0 M, highlighting stable first solvation shell peaks at approximately 2.42 Å for Ca-O(TFSI) and for Ca-O(PC) . Right panels show the corresponding cumulative coordination numbers computed by integrating the RDFs up to distance r , with vertical dashed lines indicating the first solvation shell boundaries at 3.25 Å (Ca-O(TFSI)) and 3.00 Å (Ca-O(PC)).

composition at different concentrations is shown in Figure 3.20.

The analysis reveals that at low concentrations (0.1–0.3 M), calcium’s first solvation shell is dominated by configurations with a high number of coordinated PC (typically 4–7) and one or no TFSI molecules (0–1). The predominant coordination motifs are (0 TFSI, 7 PC), (1 TFSI, 5 PC), and (1 TFSI, 4 PC), while the (2 TFSI, 2 PC) configuration emerges only at 0.3 M. Together, these arrangements account for more than 50% of all observed coordination events.

As concentration increases (0.4–0.7 M), there is a progressive increase in TFSI molecules coordination, with common configurations shifting to (1 TFSI, 4 PC), (2 TFSI, 3 PC), and (1 TFSI, 5 PC). During this range, the total number of coordinating oxygen atoms remains approximately constant, indicating a gradual substitution

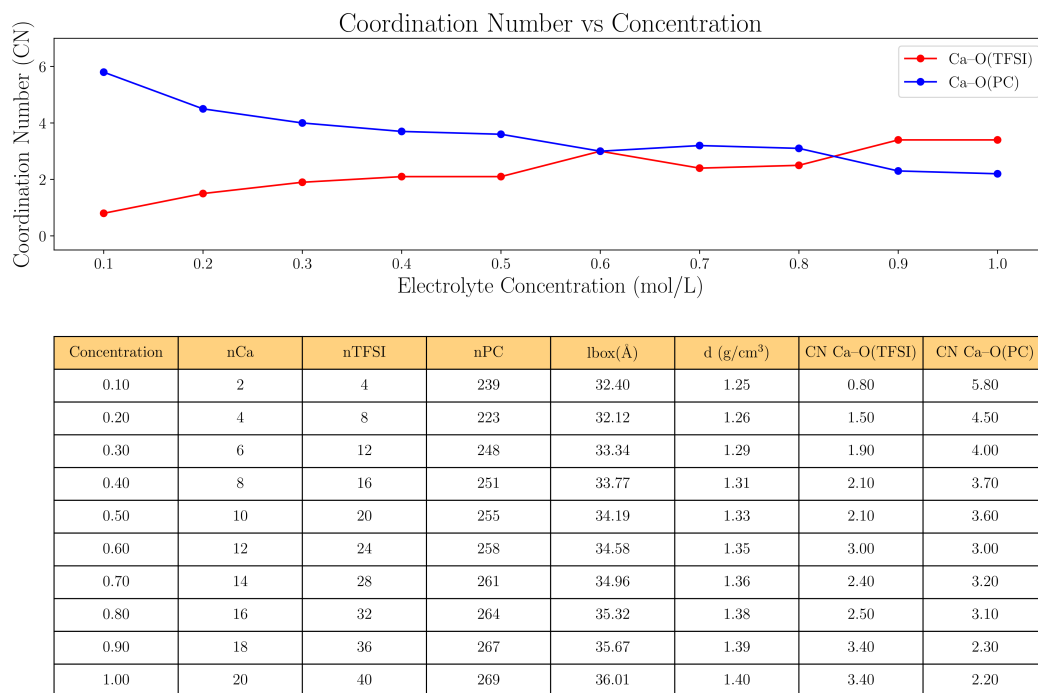


Figure 3.19 Coordination numbers of Ca^{2+} with TFSI and PC oxygen atoms as a function of electrolyte concentration. Values are extracted from MD simulations at each concentration using cutoff distances of 3.25 Å for Ca–O(TFSI) and 3.00 Å for Ca–O(PC), corresponding to the first minimum in their respective radial distribution functions. The data reveal a progressive shift in the coordination environment from PC-dominated to TFSI-dominated with increasing salt concentration.

of PC molecules by TFSI anions within the first solvation shell.

At higher concentrations (0.8–1.0 M), TFSI oxygen coordination becomes predominant, with frequent configurations such as (1 TFSI, 4 PC), (1 TFSI, 5 PC), (2 TFSI, 2 PC), and (2 TFSI, 3 PC). The PC contribution is significantly reduced in this regime, reflecting enhanced ion pairing and stronger calcium–anion interactions.

Less common coordination motifs are grouped in the "other" category, generally representing less than 30% of the total population.

These results highlight a clear shift in the calcium solvation shell composition as a function of electrolyte concentration, consistent with the trends observed in RDF and coordination number analyses, and demonstrate the capability of the developed polarizable force field and simulation protocol to capture the complex structural behavior of calcium solvation in $\text{CaTFSI}_2/\text{PC}$ electrolytes.

To compare the results of polarizable molecular dynamics simulations with experimental spectroscopic data, the coordination environment of calcium ions with PC and TFSI was analyzed. In simulations, the fraction of calcium atoms coordinated by each species was calculated through a dedicated workflow implemented with a hybrid Bash–Tcl script in the VMD software [100]. For each trajectory frame, all residues within the first solvation shell of each calcium ion were identified, where the boundary of the first shell was defined by the cutoff distance obtained from the RDFs. The number of calcium ions coordinated by TFSI and the number coordi-

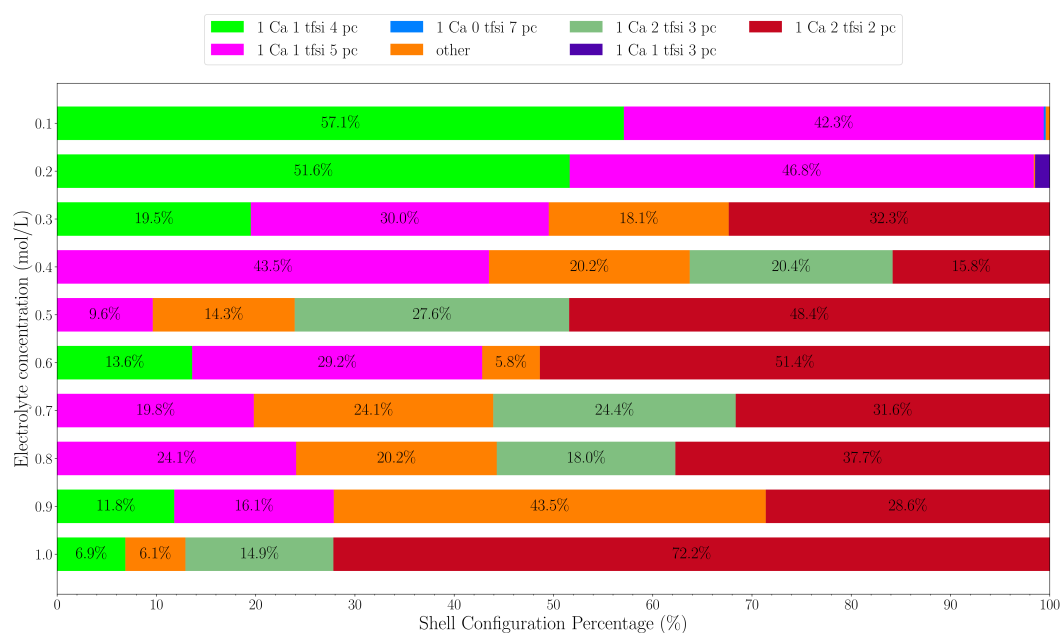


Figure 3.20 Percentage Composition of the first solvation shell of Ca^{2+} in $\text{CaTFSI}_2/\text{PC}$ solutions at various electrolyte concentrations. The most frequent configurations, classified by the number of TFSI and PC molecules coordinated to calcium, are reported as percentage. The "other" category groups less frequent configurations.

nated exclusively by PC were then counted and normalized by the total number of calcium ions in the simulation box, yielding the instantaneous coordination fractions. Average coordination fractions at each concentration were obtained by averaging these normalized values over the equilibrated portion of the trajectories.

Experimental coordination indicators were extracted from Raman spectroscopy. Specifically, the relative areas of characteristic vibrational bands associated with PC and TFSI coordination were analyzed (Figure 3.5, left). These spectral areas provide apparent coordination fractions, as they implicitly assume comparable Raman response factors (cross-sections) for the vibrational modes considered. While not strictly equivalent to molar coordination fractions, such area ratios can be used as semi-quantitative markers of coordination environments. A conservative 10 % error on the total area was applied, implemented by introducing a 10 % relative uncertainty on each band area and propagating it to the fractional quantities via standard derivative-based error-propagation, to account for uncertainties in spectral deconvolution and in the equal-cross-section assumption.

Figure 3.21 presents the comparison between Raman-derived apparent fractions and simulation-based coordination fractions across $\text{Ca}(\text{TFSI})_2$ concentrations from 0.1 to 1.0 M. Computational results and their standard deviations were obtained through statistical analysis of the coordination fractions from the MD trajectories.

At low concentrations (0.1–0.3 M), both experiment and simulation indicate that calcium is predominantly coordinated by PC, with fractions exceeding 0.65 and TFSI fractions below 0.35. The simulations tend to slightly overestimate PC coordination relative to Raman data, but values remain consistent within error bars. At

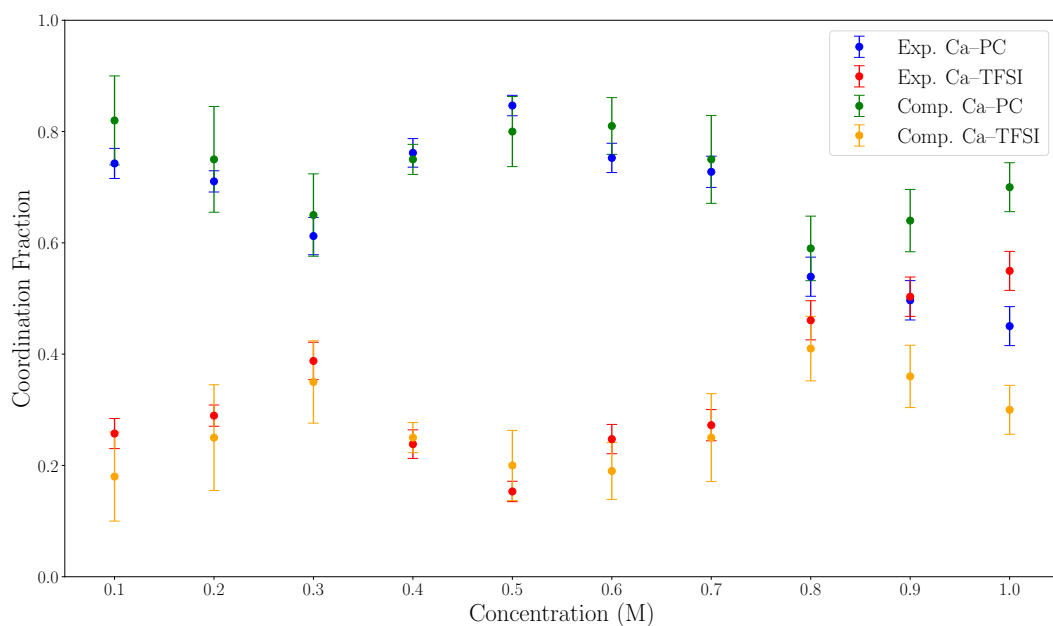


Figure 3.21 Comparison between Raman-derived apparent coordination fractions and coordination fractions from polarizable molecular dynamics simulations as a function of CaTFSI_2 concentration in PC. Coordination fractions to PC (green and blue markers) and TFSI (orange and red markers) are shown for experiments and simulations. Error bars represent propagated measurement errors (experiments) and standard deviations (simulations). Both approaches indicate a concentration-dependent shift from PC-dominated to TFSI-dominated coordination.

higher concentrations, a clear shift occurs, with TFSI coordination increasing and PC coordination decreasing, reflecting enhanced ion pairing and the displacement of solvent molecules by anions in the first solvation shell. Quantitatively, at 1.0 M, Raman analysis suggests an apparent distribution of 45% PC and 55% TFSI coordination, whereas simulations yield 69% PC and 31% TFSI fractions. This discrepancy may arise from both the limitations of the force field in describing ion pairing dynamics and the simplifying assumption of equal Raman cross-sections underlying the experimental analysis.

To further illustrate the distribution and statistical variation of simulation results, Figure 3.22 shows bar plots of the mean fractions with error bars corresponding to the standard deviation calculated over trajectory frames at each concentration.

In summary, the combined analysis confirms that polarizable MD simulations reproduce the experimentally observed concentration-dependent shift in calcium solvation shell composition. The agreement is particularly good at low concentrations, while the quantitative differences observed at high concentration likely reflect both experimental approximations and current limitations in the force field description of ion pairing. Nevertheless, the overall qualitative consistency supports the reliability of the simulation methodology and provides valuable guidance for further refinement of both experimental analysis and computational modeling.

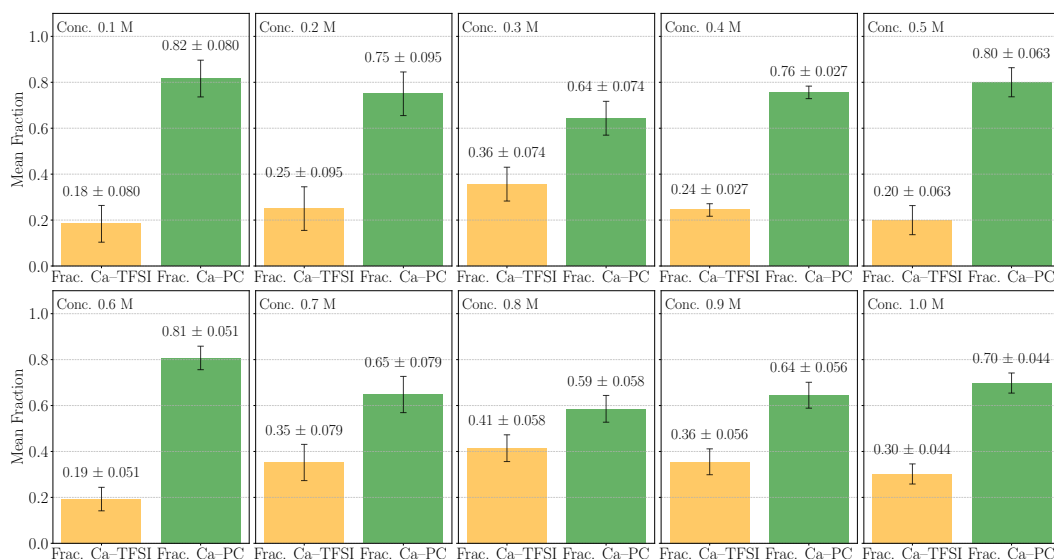


Figure 3.22 Mean fractions of calcium coordination by TFSI and PC oxygen atoms obtained from polarizable molecular dynamics simulations at various concentrations. Each subplot corresponds to a specific concentration (0.1 to 1.0 M). Bars indicate mean coordination fractions, and error bars denote the standard deviation over trajectory frames, highlighting the dynamic nature of calcium’s solvation environment.

3.8 Concluding Remarks and Future Directions

This chapter has presented a comprehensive characterization of calcium ion solvation in CaTFSI₂/propylene carbonate electrolytes, employing computational methods, particularly, classical and polarizable, molecular dynamics simulations, complemented by quantum mechanical parameter refinements and validated against experimental Raman spectroscopy. The results elucidate how polarization effects critically influence the solvation structure, improving agreement with experimental coordination numbers and radial distribution functions compared to classical fixed-charge models. As demonstrated in Section 3.7, the use of AMOEBA polarizable force fields refined with calcium polarizability parameters computed via high-level DLPNO-MP2 calculations yielded radial distribution functions (Figure 3.17) with first solvation shell peak distances and coordination numbers that approach better the experimental values for calcium in water [97, 98]. This improvement highlights the essential role of explicit polarization in capturing the strong electrostatic interactions between Ca²⁺ and coordinating oxygen atoms.

The concentration-dependent evolution of the calcium solvation environment in the CaTFSI₂/PC electrolyte was analyzed in detail through simulations at various molarities. The radial distribution functions and coordination numbers presented in Figures 3.18 and 3.19 reveal a clear shift from a PC-dominated coordination shell at low concentrations to increased TFSI coordination at higher concentrations. This transition was further supported by the solvation shell composition analysis shown in Figure 3.20, which quantified the gradual replacement of solvent molecules with anions in calcium’s first coordination shell. Finally, calcium was found to coordinate, at an average distance of 2.42 Å, with approximately 5–7 oxygen atoms, depending

on the solution concentration, forming the basis for comparison with experimental coordination fractions discussed below.

Critically, the fractions of calcium coordination by PC and TFSI oxygen atoms computed from the simulations exhibited good qualitative agreement and reasonable quantitative correspondence with Raman spectroscopy-derived fractions, as shown in Figure 3.21. The error bars calculated from trajectory fluctuations and experimental uncertainty demonstrate that the polarizable force field reliably captures the dynamic solvation behavior across a broad concentration range, validating the adopted modeling and analysis protocols.

It is important to note, however, that Raman-derived fractions are based on relative band areas and thus represent apparent coordination indicators, implicitly assuming comparable Raman cross-sections for the selected vibrational modes. Simulations, in contrast, provide absolute coordination numbers from geometric criteria. The very good agreement in the concentration-dependent trends between the two approaches supports the validity of the developed force field, while the differences observed at higher concentration reflect both experimental approximations and the intrinsic challenges of modeling ion pairing in concentrated electrolytes.

Nonetheless, small discrepancies observed at the highest concentrations, where simulations tend to slightly overestimate PC coordination relative to experiment, indicate avenues for future improvement. These may include enhanced force field refinement to better model ion pairing and cluster formation, longer simulations to improve sampling of rare coordination states, and consideration of charge transfer effects.

In conclusion, the integration of polarizable molecular dynamics with carefully derived quantum mechanical parameters and experimental validation provides a reliable framework to study calcium solvation in complex electrolytes. This approach not only advances fundamental understanding but also offers practical guidance for the design of optimized electrolyte formulations in calcium-based energy storage technologies. Future work extending this methodology to diverse solvent and salt combinations will be instrumental in advancing multivalent ion battery research.

Chapter 4

Analysis and recycle of spent LiFePO_4 batteries electrolytes

Chapter Overview

This chapter addresses the recycling and characterization of electrolytes from spent LiFePO_4 (LFP) batteries. The workflow includes safe disassembly of industrial SNAM pouch cells and recovery of the LFP/FP cathode material, followed by fabrication of coin half-cells using the recycled powders. These cells were subjected to controlled electrochemical cycling protocols to generate electrolytes at different aging stages. Electrochemical testing enabled the evaluation of capacity fade and polarization growth under various operating conditions, providing direct evidence of electrolyte degradation and interfacial instability. Extracted electrolytes were then analyzed by gas chromatography–mass spectrometry (GC–MS) and Fourier transform infrared (FT–IR) spectroscopy, complemented by classical molecular dynamics and quantum chemical simulations. This integrated approach allowed the identification of key degradation pathways and molecular species, such as phosphate related species (eg. trifluorophosphate (TFP)) and ether/glycol-derived species (eg. diethylene glycol dimethyl ether (DEG–DME)), that emerge during cycling and environmental exposure. By combining electrochemical performance metrics with spectroscopic and computational analyses, the chapter provides a comprehensive view of electrolyte evolution during battery recycling, establishing both methodological guidelines and mechanistic insights that are essential for improving the sustainability and efficiency of lithium-ion battery reuse.

4.1 Preparation of LFP Material from Spent SNAM Pouch Cells

The SNAM Industry provided a batch of spent batteries, specifically pouch cells. These cells consisted of a soft aluminum metal casing, selected for its flexibility and suitability to fit confined spaces. Inside, multiple electrode layers were present, each composed of a rectangular aluminum foil uniformly coated on both sides with an electrode slurry. This slurry, for cathode, consisted of LiFePO_4 and graphite

particles bound together by a polymeric binder based on polyvinylidene fluoride (PVDF).

Each electrode layer was enclosed within a permeable plastic pouch acting as a separator. The assembly was impregnated with LP30 electrolyte, a 1 M solution of LiPF_6 in a 50:50 v/v mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). The molecular structures of the electrolyte components are shown in Figure 4.1.

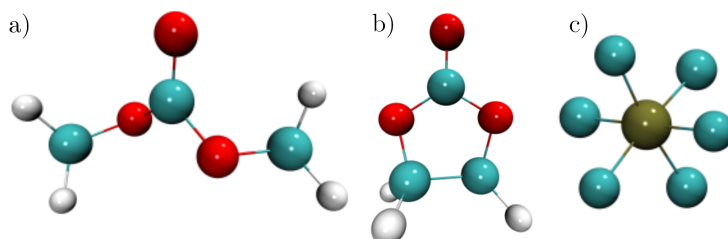


Figure 4.1 Representations of the molecular species constituting the LP30 electrolyte: (a) dimethyl carbonate (DMC), (b) ethylene carbonate (EC), and (c) hexafluorophosphate anion (PF_6^-).

The spent cells were initially opened inside a glove box filled with argon atmosphere (O_2 and $\text{H}_2\text{O} < 1$ ppm) to minimize exposure to moisture and atmospheric oxygen. The electrodes were carefully separated and subsequently stored under the same inert atmosphere to prevent any undesired reactions with the external environment. From the recovered materials, 32 LFP/FP electrodes were selected. These were removed from the glove box, cut into two equal parts, and deliberately exposed to uncontrolled ambient atmosphere for varying durations: 0 minutes, 30 minutes, 1 hour, 1 hour 30 minutes, 2 hours, 3 hours, 4 hours, and 5 hours. For each exposure interval, four electrode samples were taken. At the end of each exposure time, the four electrode pieces were immersed in a beaker containing triethyl phosphate (TEP) heated to 100 °C. This procedure allowed complete delamination of the active materials from the current collector. Subsequently, the resulting fragments were removed from the beaker, washed with ethanol to remove any residues, and then thoroughly dried. Once dried, the cathode film was finely ground to obtain a homogeneous powder. This material was then used for subsequent characterization and analysis. Although the exact cathode composition could not be precisely determined, it was estimated, based on technical datasheets provided by the industry and confirmed through electrochemical tests, that approximately 92% of the material consists of iron-based compounds (LiFePO_4 and FePO_4), with an approximate $\text{LiFePO}_4/\text{FePO}_4$ ratio of 70:30. The remaining 8% was identified as conductive carbon and a PVDF binder. This procedure ensures the safe and controlled handling of spent electrodes and enables the recovery of the LFP/FP active material while preserving its physicochemical properties for subsequent reuse or recycling. Moreover, exposure to different ambient times and TEP treatment enables assessment of the influence of environmental atmosphere and temperature on both the delamination process and the properties of the recovered material.

4.2 Preparation Procedure of Coin Half-Cells from Recycled LFP/FP Powder

Following the recovery of the recycled LFP/FP active material, a new electrode slurry was prepared for the fabrication of coin cells. The slurry composition was based on the following weight percentages: 90% recycled $\text{LiFePO}_4/\text{FePO}_4$, 5% conductive carbon C65, and 5% polymeric binder solution.

The first two components were weighed, after which the polymeric binder solution, composed of PVDF dissolved in N-methyl-2-pyrrolidone (NMP) at a 10:90 weight ratio, was added. Additional NMP, serving as a viscosity modifier, was gradually introduced during mixing using a mechanical stirrer. NMP was added incrementally until a homogeneous slurry with an appropriate viscosity was obtained.

The prepared slurry was uniformly coated onto an aluminum foil substrate heated to 80 °C using a doctor blade moving at 20 mm/s, aiming for a wet film thickness of 200 μm . The coated electrode layer was then dried in an oven at 80 °C for 4 hours to ensure complete evaporation of the NMP solvent and to promote proper adhesion between the LFP/FP particles and the conductive carbon C65.

Once the solvent had fully evaporated, electrodes with a diameter of 12 mm were punched out, with an average active material loading of 1.35 mg/cm^2 . Prior to transfer into the glove box, the electrodes underwent further drying in a büchi at 100 °C for 3 hours.

Coin half-cell assembly was conducted inside a glove box under controlled atmosphere, employing lithium metal as the anode, a Whatman separator, and 800 μL of LP30 electrolyte (Sigma-Aldrich, product 746711). The assembled cells were subsequently subjected to electrochemical testing, with cycling parameters systematically varied to evaluate performance and to study electrolyte aging.

4.3 Cycling Procedure of Coin Cells Using Recycled LFP and Sample Preparation

To evaluate the recycled material and to obtain electrolyte samples at different aging stages, the prepared coin cells were cycled on a Neware battery tester following various protocols. Each protocol included an initial activation phase aimed at forming a uniform and stable solid electrolyte interphase (SEI) at the anode interface.

The activation phase consisted of several charge-discharge cycles within a voltage window of 3.8 V (charge) to 2.5 V (discharge) at the following C-rates: 0.1 C for 5 cycles, 0.2 C for 5 cycles, 0.5 C for 10 cycles, and 1 C for 10 cycles.

Following activation, six different aging conditions were tested. The first four protocols focused on evaluating the electrolyte by subjecting the cells to charge-discharge cycling at 2 C for the following number of cycles: 2, 10, 100, and more than 100 but fewer than 500. The last two protocols consisted of 100 cycles at 2 C followed by 2 cycles at 0.1 C, and 10 charge cycles at 1 C with discharge cycles at progressively increasing C-rates from 1 to 5 C.

Upon completion of the aging protocols, the cells were opened inside a glovebox, and the electrolyte-soaked separator was extracted. Each separator was then divided into two parts: one portion was placed in a vial for GC-MS analysis, where acetonitrile

(ACN) was added to fill the vial and left to extract for 24 hours. The other portion was sandwiched between two glass slides, secured with clamps to slow electrolyte evaporation.

The separator samples held between the glass slides were subsequently removed and analyzed at ambient atmosphere via Fourier Transform Infrared (FT-IR) spectroscopy using a Thermo Scientific Nicolet iS50 FT-IR spectrometer. Spectra were collected with 64 scans at a spectral resolution of 4 cm^{-1} . This acquisition protocol was chosen to optimize spectral quality and resolution while minimizing acquisition time, since prolonged exposure to ambient atmosphere would cause complete evaporation of the electrolyte, particularly the more volatile dimethyl carbonate (DMC).

The vials containing the separators after 24 hours of extraction were used for GC-MS analysis. A SHIMADZU SH-200MS capillary column (30 m length $\times$ 0.25 mm internal diameter, 0.25 μm film thickness) coated with crossbond trifluoropropylmethyl polysiloxane was employed, mounted on a Shimadzu GC-MS instrument. The temperature program started at $40\text{ }^{\circ}\text{C}$, held for 3 minutes, followed by a ramp of $8\text{ }^{\circ}\text{C}/\text{min}$ up to $280\text{ }^{\circ}\text{C}$, held for 5 minutes, with a total run time of 38 minutes. The injection port temperature was set to $250\text{ }^{\circ}\text{C}$ in split mode. Helium was used as the carrier gas in flow control mode with a linear velocity. The AOC-20 autosampler was configured to perform two rinses of the sample with ACN, one before and one after the run, using high piston speeds for aspiration and injection.

4.4 Electrochemical Performance and Aging Analysis of Recycled LFP Cells

The electrochemical performance of coin cells assembled with recycled lithium iron phosphate (LFP) material was systematically evaluated under six distinct cycling protocols, as detailed in Section 4.3, to investigate electrolyte aging and overall cell stability. Figures 4.2 and 4.3 display comparative discharge capacities for the protocols tested.

At a low number of cycles at 2 C, specifically 2 and 10 cycles, the cells yielded average capacities of approximately 1.15 mAh/g and 0.89 mAh/g, respectively, with low standard deviations (0.02 mAh/g), indicating consistent and reproducible performance. After 100 cycles at 2 C, the capacity decreases, though less markedly than in the 2-cycle and 10-cycle cases; however, the number of cells tested was lower. The average capacity reached about 10.82 mAh/g, with a higher standard deviation of 10.05 mAh/g compared to the other two cases, indicating substantial variability among the cells.

Extended cycling beyond 100 but fewer than 500 cycles led to a further decrease in capacity, eventually stabilizing at approximately 0.02 mAh/g. This behavior is consistent with a rapid initial degradation of the solid-electrolyte interphase (SEI), followed by the establishment of a more stable interphase whose slower evolution limits further capacity loss.

Protocols incorporating lower C-rate cycling following high-rate steps, such as 100 cycles at 2 C plus 2 cycles at 0.1 C, showed slight capacity recovery (97.55 mAh/g). Conversely, cells cycled at 1 C rate of charge and with discharge rates progressively increasing to 5 C experienced more pronounced capacity decline (17.81 mAh/g),

underscoring the impact of high-rate stress on cell performance.

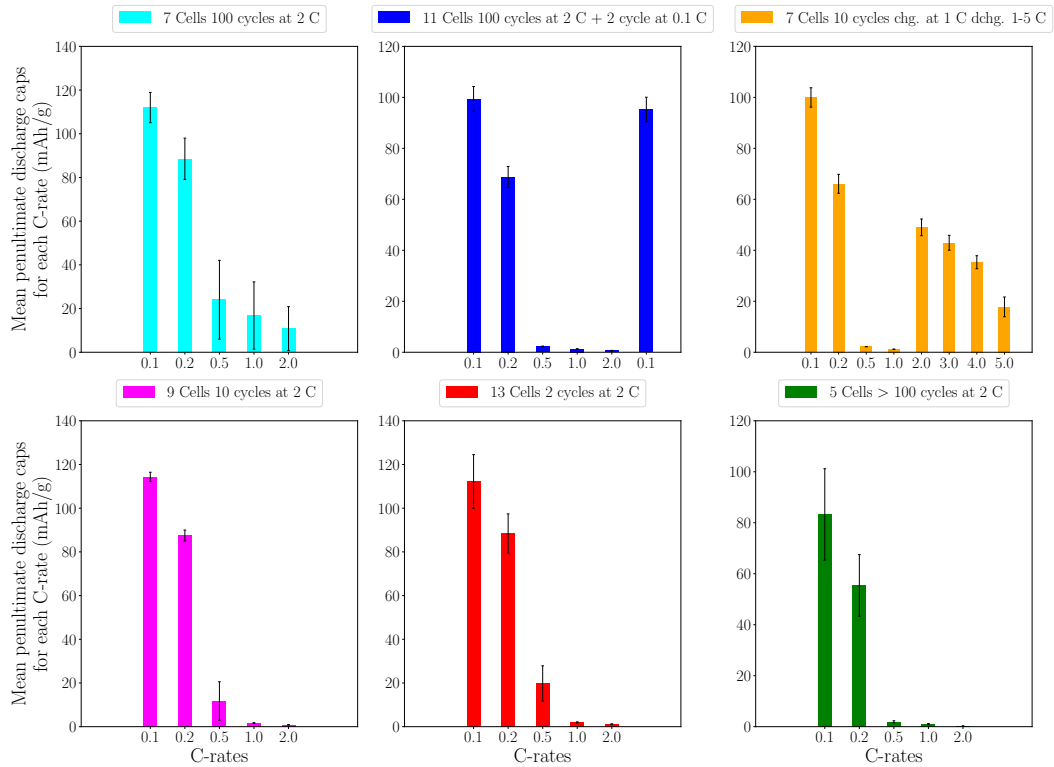


Figure 4.2 Bar chart comparing the average penultimate discharge capacities at each C-rate for recycled LFP coin cells subjected to different cycling protocols. Error bars represent standard deviations across replicate cells.

Complementary to the capacity measurements, Figures 4.4 and 4.5 present polarization data indicative of internal resistance and charge-transfer kinetics. In the early cycling stages, polarization values were close to 0.25 mV after 2 cycles at 2 C, consistent with a substantial capacity loss and suggesting significant kinetic limitations, likely associated with increased interfacial impedance from initial SEI formation or degradation. As cycling progressed, polarization approached approximately 0.5 mV at 10 and 100 cycles, reflecting increasing resistive losses and interfacial degradation. Cells cycled for more than 100 cycles exhibited higher polarization, around 0.7 mV, paralleling the observed capacity stabilization and suggesting the attainment of a degradation–recovery equilibrium at the electrode–electrolyte interface. Protocols that incorporated low C-rate cycling after high-rate steps exhibited low polarization values consistent with a partial recovery in capacity.

The highest polarization values (0.92 mV) occurred in cells subjected to rapidly increasing discharge rates up to 5 C, underscoring the detrimental impact of aggressive cycling conditions on electrode kinetics and electrolyte stability.

Statistical analysis of replicate measurements confirms good reproducibility, with standard deviations typically within 5% of mean values for both capacity and polarization. This reliability strengthens the confidence in the observed aging trends.

In conclusion, the combined capacity and polarization data demonstrate that while

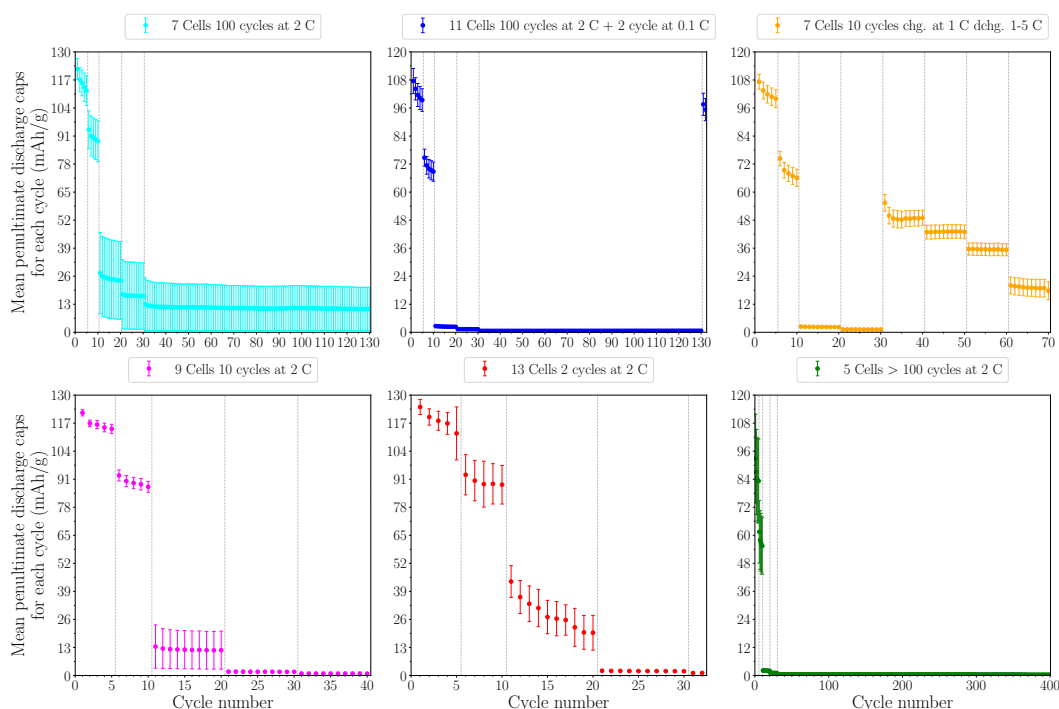


Figure 4.3 Scatter plot of mean penultimate discharge capacities as a function of cycle number for various cycling protocols applied to recycled LFP coin cells. The straight lines represent the C-rate boundaries, while the error bars indicate the standard deviation across replicates.

initial cycling at low C-rates maintains near-theoretical capacity and low resistive losses, prolonged and high-rate cycling accelerate capacity fade and increase polarization. These findings are consistent with progressive electrolyte degradation and interfacial instability. Although the absolute capacity values measured in these recycled LFP cells are markedly low, they are acceptable in the present context, as the primary objective of this study is to investigate electrolyte aging rather than to optimize electrode performance. The electrochemical results therefore provide essential context for interpreting the spectroscopic and molecular insights into electrolyte aging presented in subsequent sections.

4.5 GC-MS Analysis of Aged Electrolytes from Recycled LFP Cells

Gas Chromatography–Mass Spectrometry (GC-MS) analysis was conducted on electrolyte samples extracted from coin cells cycled under various aging protocols. The samples consisted of separators soaked with electrolyte, which were immersed in acetonitrile (ACN) for 24 hours inside a glovebox to extract soluble components. Following extraction, the solutions were analyzed using a SHIMADZU GC-MS system equipped with a SHIMADZU-200MS capillary column coated with crossbond trifluoropropylmethyl polysiloxane. The temperature program started at 40 °C (held 3 minutes), ramped at 8 °C/min to 280 °C (held 5 minutes), with Helium as carrier

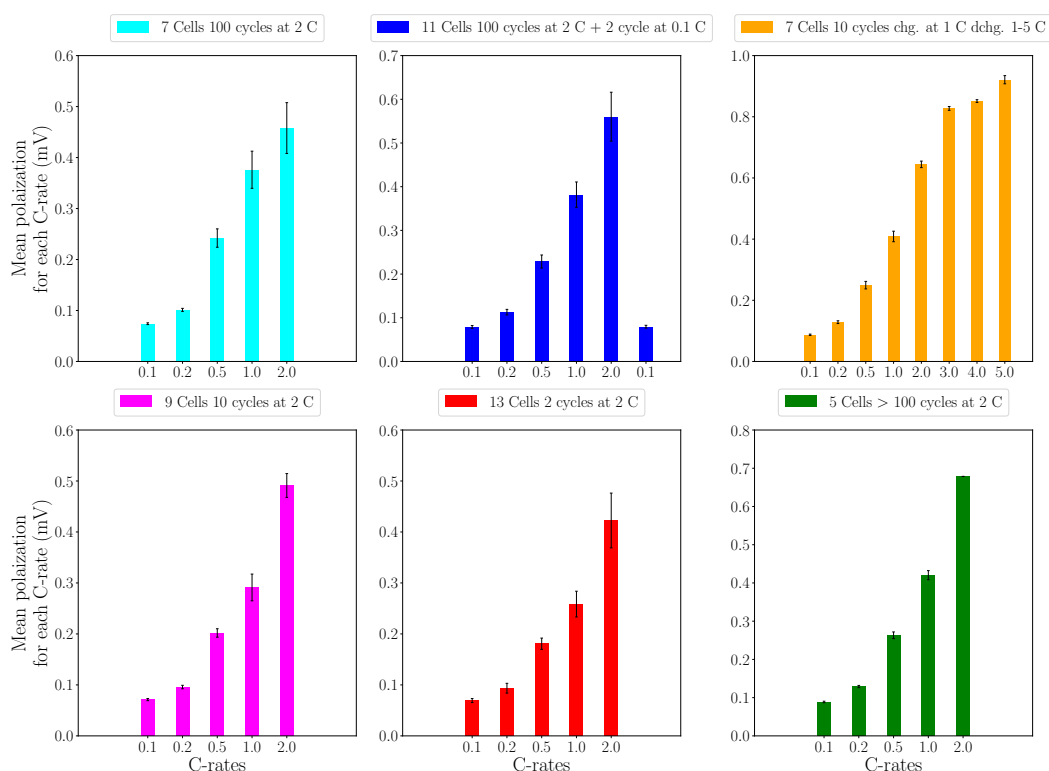


Figure 4.4 Bar chart comparing the average polarization values for each C-rate, of recycled LFP coin cells under various cycling protocols. Error bars represent standard deviations across replicates.

gas and split injection mode at 250 °C, as detailed in the experimental methods section 2.5.

Figure 4.6 shows the overlay of average GC-MS chromatograms for the different aging protocols, compared with the reference sample extracted from non-cycled cells (only closed and opened). The chromatograms are plotted as normalized intensity versus retention time with a split axis (break) to highlight both early and late eluting species. The shaded areas around the lines represent standard deviations among replicate measurements, providing an indication of reproducibility.

Quantitative integration of the peak areas within the DMC (3.00–3.25 min) and EC (13.50–14.00 min) retention time windows reveals changes in the relative abundance of these solvent components with aging. The ratio $A(\text{DMC})/A(\text{EC})$ remains approximately constant across different cycle numbers and conditions, with an average value of about 0.5. This indicates that dimethyl carbonate is depleted roughly twice as fast as ethylene carbonate, but that both solvents follow comparable relative trends under the tested conditions, without evidence of preferential degradation pathways emerging during cycling. It should also be considered that the higher volatility of dimethyl carbonate could contribute to its apparent depletion through evaporation during handling, and thus a fraction of the observed loss may not solely arise from electrochemical processes. Furthermore, the chromatographic peak shapes remain largely consistent, with cycling primarily affecting peak area and intensity, reflecting

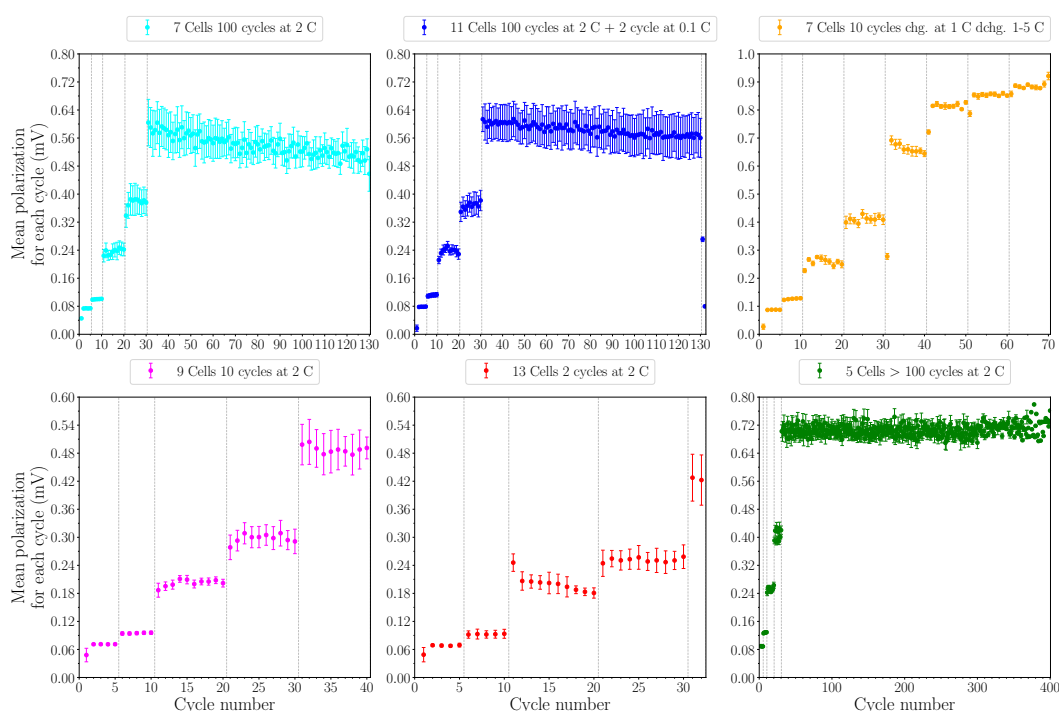


Figure 4.5 Scatter plot of mean polarization values versus cycle number for the different cycling protocols applied to recycled LFP coin cells. The straight lines represent the C-rate boundaries, while the error bars indicate the standard deviation across replicates.

changes in solvent concentration rather than alterations in profile or the emergence of overlapping species. These results are consistent with electrochemical evidence for electrolyte decomposition and evolving solvation environments.

In addition to solvent depletion, two dominant classes of degradation products emerge during cycling and upon ambient exposure. The first are phosphate-related species, such as trifluorophosphate (TFP), which signify salt decomposition and subsequent reaction cascades involving the conducting salt anion (PF_6^-). The second group comprises ether- and glycol-derived species, exemplified by diethylene glycol dimethyl ether (DEG–DME), which likely originate from solvent fragmentation and recombination processes under electrochemical and oxidative conditions.

The concurrent presence of these products underscores the multifaceted chemistry of electrolyte degradation, wherein both salt-derived and solvent-derived species accumulate. Their detection complements the solvent depletion trends, confirming that electrolyte aging involves not only quantitative solvent loss but also the generation of chemically distinct secondary products that can substantially modify the physicochemical environment of the electrolyte.

Together, the GC–MS data provide molecular-level insight into the chemical evolution of the electrolyte during cycling, complementing the capacity and polarization analyses. The relatively constant DMC/EC ratio, along with systematic reductions in chromatographic peak area and intensity, reflects progressive but proportionate solvent depletion. These molecular-level alterations are likely to contribute to the observed capacity fade and increased polarization in aged cells.

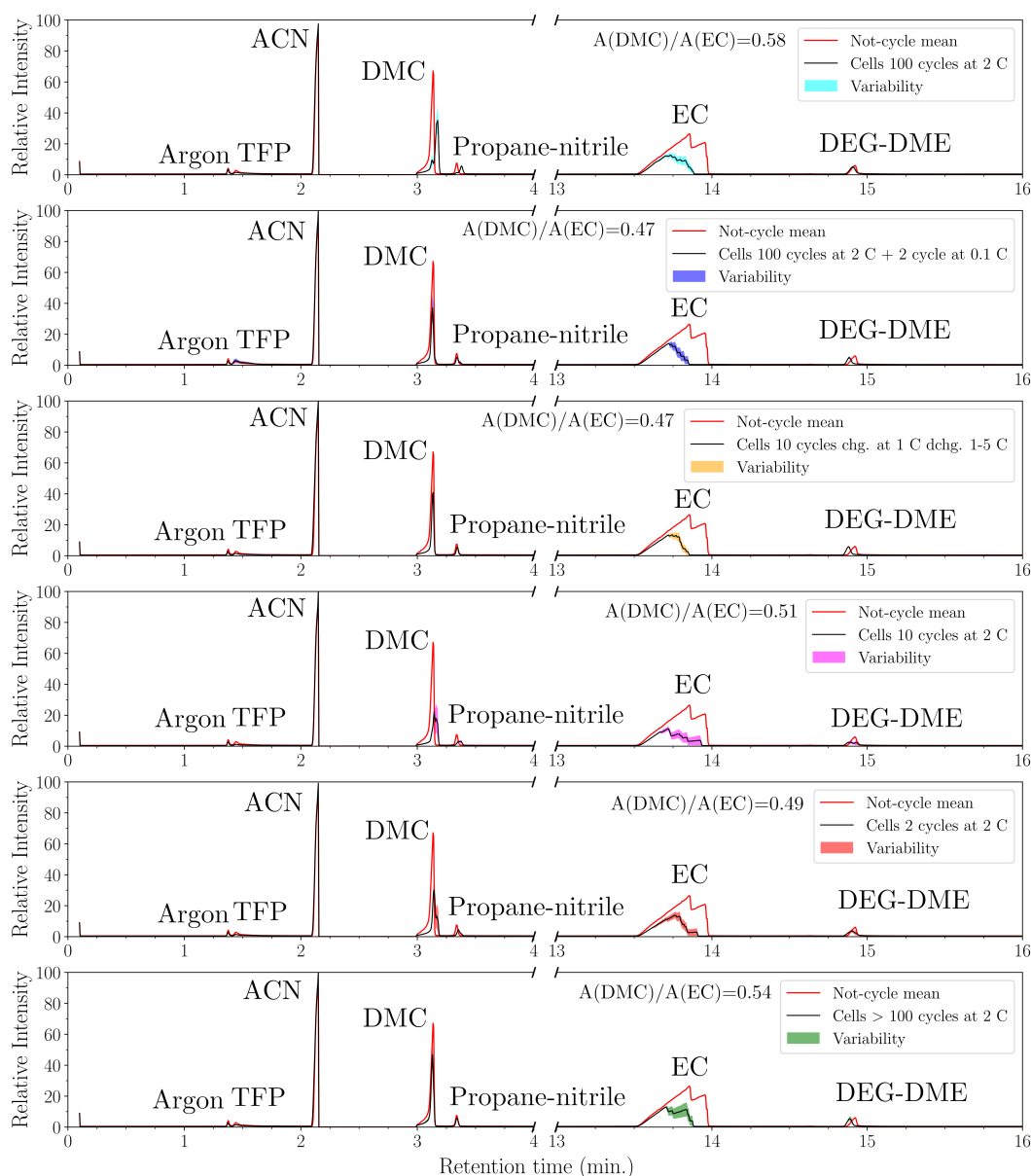


Figure 4.6 Overlay of average GC-MS chromatograms of electrolyte extracts from recycled LFP coin cells subjected to different cycling-induced aging protocols. The chromatograms are normalized and plotted as a function of retention time, with shaded regions indicating the standard deviation across replicate measurements. The ratio between the chromatographic peak areas of dimethyl carbonate, $A(\text{DMC})$, and ethylene carbonate, $A(\text{EC})$, remains approximately constant with aging, with an average value of about 0.5. This indicates that DMC is depleted roughly twice as fast as EC, while both solvents exhibit comparable relative trends under the tested cycling conditions. In addition to the solvent peaks, characteristic signals corresponding to degradation products such as phosphate-related species (e.g., trifluorophosphate, TFP) and ether/glycol-derived species (e.g., diethylene glycol dimethyl ether, DEG-DME). A split x-axis is used to highlight both early- and late-eluting components for improved visualization.

4.6 IR Spectra Analysis of Electrolytes from Recycled LFP Cells

The experimental spectra, collected as described in Section 4.3, were baseline-corrected using a custom Python script developed for interactive and flexible background removal. Characteristic background points were manually selected for each spectrum, enabling precise marking along the signal. These points were then used to fit a baseline curve by piecewise linear interpolation, chosen for its ability to approximate the steeply varying background typical of infrared (IR) spectra collected in ambient atmosphere. For pristine electrolyte spectra interpretation and vibrational band assignment, IR spectra were simulated based on first solvation shell clusters extracted from classical molecular dynamics (MD) simulations of the electrolyte system. The bulk electrolyte system was simulated using LAMMPS [96], following the protocol described in Section 3.5. It comprised 5 Li^+ ions, 5 PF_6^- anions, 29 DMC molecules, and 36 EC molecules confined within a cubic box with edge length 20.30 Å. The initial configuration was generated using Packmol [95] with a tolerance of 2.5 Å, which approximates the typical LP30 electrolyte composition (1 M LiPF_6 in EC/DMC 50:50 v/v).

The parameters for Li^+ ions were taken from the Lennard-Jones set developed by Li and Merz [76], optimized to reproduce the hydration structure of Li^+ in SPC/E water under Ewald summation. The adopted values were $\varepsilon=0.011468$ kJ/mol and $\sigma=2.24$ Å, consistent with the SPC/E water model. For the PF_6^- anion, parameters were taken from the OPLS-AA force field refined for ionic liquids [69], while for EC and DMC the OPLS-AA force field for organic molecules was used [68]. The resulting simulated density of 1.30 g/cm³ is in excellent agreement with the experimental value, confirming the reliability of the chosen parametrization.

The radial distribution functions (RDFs), and the corresponding coordination numbers $\text{CN}(r)$, for lithium interactions with carbonyl oxygen atoms of DMC and EC, as well as fluorine atoms of the PF_6^- anion, were computed from the MD simulation. These are shown in Figure 4.7.

The first sharp peak in the RDFs for Li–O(DMC) and Li–O(EC) correspond to a coordination distance of 1.98 Å. The $\text{CN}(r)$ integrated up to the cutoff distance of 3.00 Å reveals an average coordination number close to 3 for EC carbonyl oxygens and about 2 for DMC carbonyl oxygens, consistent with mixed solvation shell environments: in one case, lithium is coordinated by approximately three EC molecules and one DMC molecule, while in the other case it is coordinated by about two DMC and two EC molecules. Less frequently, additional configurations were also observed in which lithium was coordinated by three DMC molecules and one EC molecule. Similarly, the Li–F(PF_6) RDF exhibits a first peak at around 1.95 Å, reflecting the interaction between lithium ions and the fluorine atoms of the PF_6^- anion. The corresponding coordination number is close to zero, but not exactly zero, indicating the presence of partial ion pairing in the electrolyte.

From the trajectory, all clusters where lithium did not coordinate to PF_6^- were extracted and categorized based on the composition of their solvation shell. For each category, the cluster with the lowest energy was selected, with energies computed using Gaussian-16 [94] and the $\omega\text{B97X-D}$ functional with Def2-TZVP basis set.

The representative lithium solvation shell clusters considered included mixed ethylene carbonate (EC) and dimethyl carbonate (DMC) compositions, namely Li-1EC-3DMC, Li-2EC-2DMC, and Li-3EC-1DMC. Clusters in which lithium was coordinated exclusively by EC or exclusively by DMC were not prioritized for vibrational analysis, since previous experimental and simulation studies indicate that Li^+ solvation in EC:DMC mixtures is typically EC-rich or mixed rather than purely single-solvent coordinated under conditions relevant to LP30 electrolytes [65, 112, 113].

Density functional theory (DFT) simulations of the IR spectra were then performed, for the three selected solvation shell clusters, using the same functional and basis set as those employed for the cluster energy evaluations. The vibrational spectra obtained from these clusters were compared with the experimental spectrum collected for the pristine electrolyte under ambient conditions, as shown in Figure 4.8.

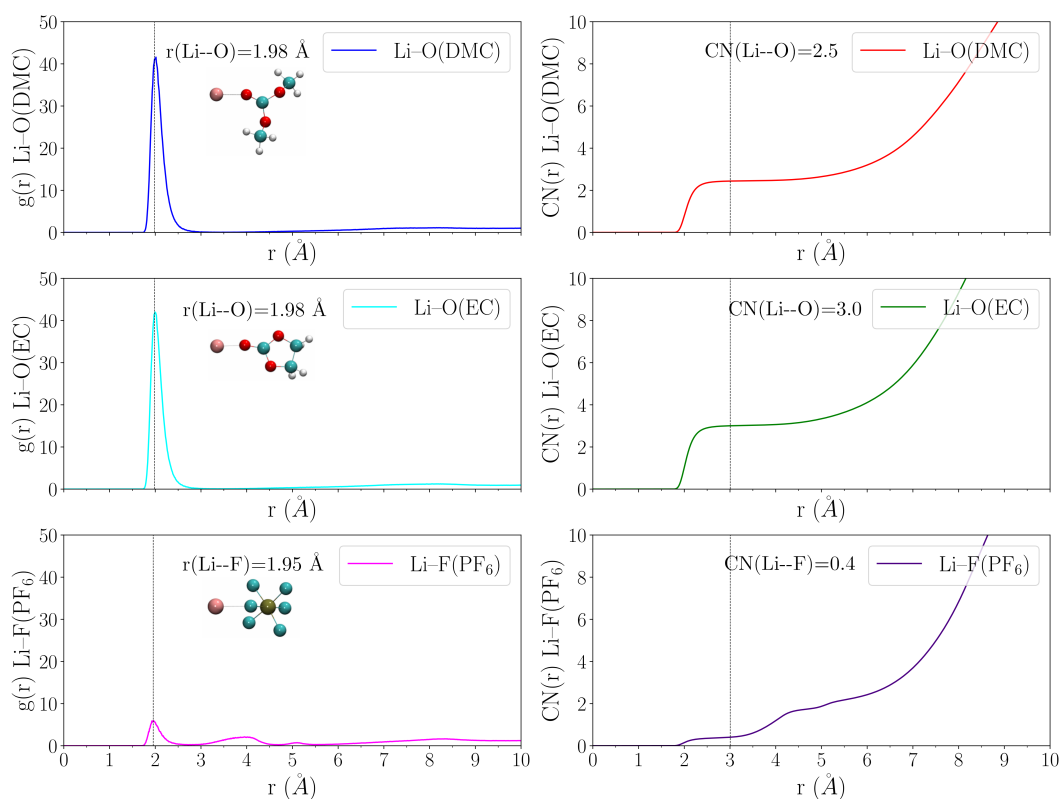


Figure 4.7 Radial distribution functions $g(r)$, and coordination numbers $\text{CN}(r)$, for lithium interactions with oxygen atoms of dimethyl carbonate (DMC), ethylene carbonate (EC), and fluorine atoms of PF_6^- anions computed from classical molecular dynamics simulations. The first peaks indicate the solvation shell structure and lithium coordination environment in the LP30 electrolyte.

The vibrational infrared spectrum of the LP30 electrolyte shows a complex pattern of overlapping bands, reflecting the variety of lithium coordination environments. The vibrational profiles derived from the simulated spectra were convoluted using Voigt line shapes (50:50 Lorentzian/Gaussian) and subsequently scaled by a factor of 0.96 to ensure alignment with the experimental data. This procedure successfully reproduces the principal features of the experimental spectrum. In the high-frequency

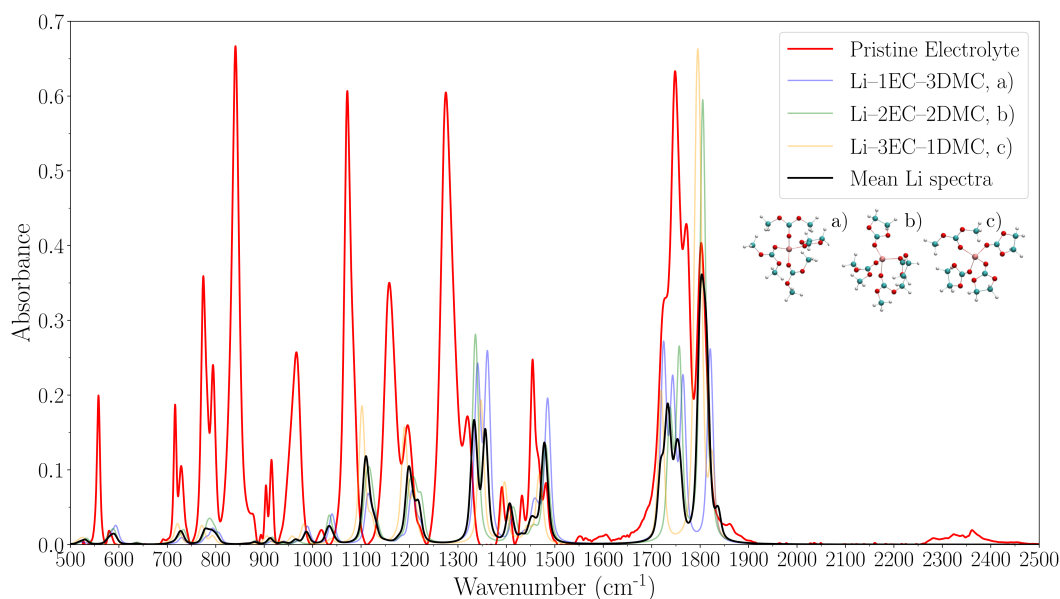


Figure 4.8 A comparison between the experimental infrared (IR) spectrum of the pristine LP30 electrolyte and the convoluted simulated spectra of representative lithium solvation-shell clusters is presented in the figure, where the clusters employed for the calculations are also depicted. The black trace corresponds to the normalized linear combination of the simulated spectra that reproduces the key experimental features.

region around 1800 cm^{-1} , the dominant band arises from the carbonyl stretching vibrations of EC and DMC molecules coordinated to lithium. This intense band is highly sensitive to the local environment, and its multimodal structure, consisting of four closely spaced peaks, reflects subtle variations in lithium–solvent interactions. Density functional theory simulations of representative coordination clusters confirm that Li^+ binds through the carbonyl oxygen atoms. The observed splitting in the carbonyl stretching region originates from differences in $\text{Li}-\text{O}(\text{C}=\text{O})$ bond strengths and coordination geometries, as well as the coexistence of distinct DMC conformers. In particular, multiple trans and cis isomers contribute, while vibrational coupling between neighboring carbonyl groups contributes further to band broadening. Together, these effects give rise to the characteristic four-peak pattern near 1800 cm^{-1} , which corresponds to carbonyl stretching modes of EC and DMC molecules in different coordination states and conformations. The consistency between the experimental spectra and the DFT-simulated vibrational profiles, shown in Figure 4.9, supports this assignment.

Between 1380 and 1540 cm^{-1} , the observed bands originate from the wagging modes of the methyl (CH_3) and ethyl (CH_2) groups of DMC and EC, respectively, which overlap with the asymmetric $\text{C}-\text{O}-\text{C}$ stretching vibrations. As shown in Figure 4.10, their intensities vary across all clusters, indicating that the aliphatic moieties change their vibrational character with changes in coordination.

In the 1240 – 1380 cm^{-1} region, the observed bands arise from the asymmetric stretching of the $\text{O}-\text{C}-\text{O}$ group of DMC. The band appears split because the contribution is associated with two different DMC isomers: the trans at lower wavenumbers and the cis at higher wavenumbers, as shown in Figure 4.11.

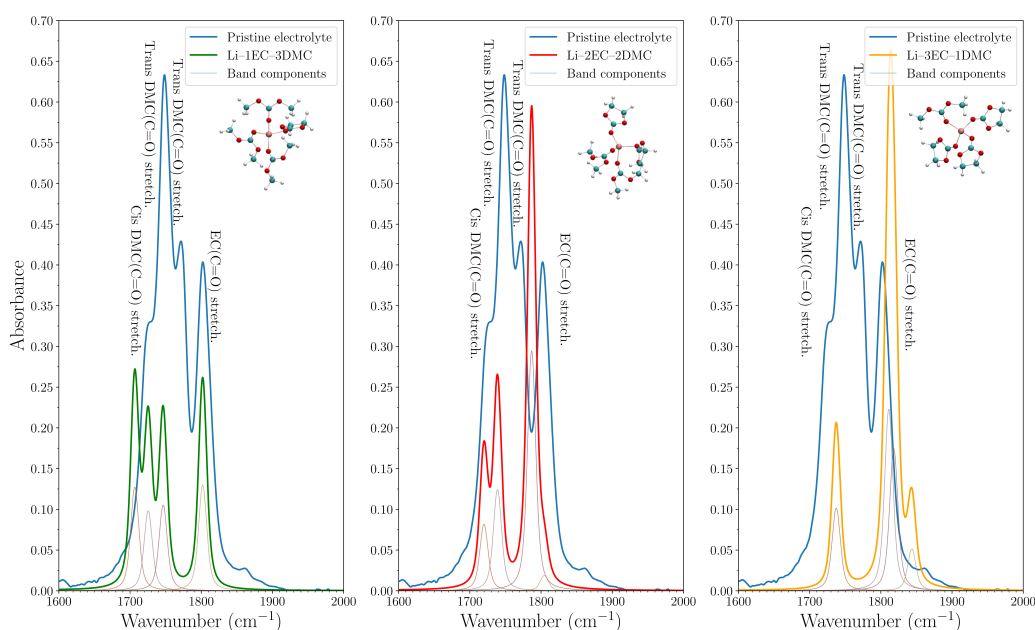


Figure 4.9 Schematic representation of IR carbonyl region and lithium coordination in the solvation shell highlighting the cis and multiple trans conformations of dimethyl carbonate (DMC). The figure illustrates the coordination of four solvent molecules (EC and DMC) to the central Li^+ ion via their carbonyl oxygen atoms, with variations in conformation and bond strength giving rise to multiple resolved carbonyl stretching peaks near 1800 cm^{-1} .

The $1150\text{--}1240\text{ cm}^{-1}$ region, shown in Figure 4.12, features vibrations associated with O–C–O stretching in the EC ring, along with contributions from the twisting motions of the $-\text{CH}_2$ groups in EC. The $1100\text{--}1150\text{ cm}^{-1}$ range corresponds to twisting modes of $-\text{CH}_2$ groups and O–C–O scissoring in EC. Finally, the $1020\text{--}1070\text{ cm}^{-1}$ region is primarily associated with $\text{CH}_3\text{--O}$ stretching combined with C–O–C bending in DMC, as well as CH_2 twisting in EC. Simulations reveal subtle variations in these modes with solvent composition, underscoring the sensitivity of carbonate structures to solvation effects.

The $900\text{--}930\text{ cm}^{-1}$ region, shown in Figure 4.13, displays vibrational bands associated with the $\text{CH}_3\text{--O--C}$ stretching of DMC, whereas the $930\text{--}1000\text{ cm}^{-1}$ range is dominated by contributions from the $\text{CH}_2\text{--CH}_2$ stretching and the O–C–O stretching of EC. Note that absolute experimental intensities are higher than those obtained from cluster simulations, as the latter do not capture bulk contributions; therefore, comparisons are based on relative trends rather than absolute absorbance.

In the low-frequency range between 700 and 750 cm^{-1} (Figure 4.14), the bands correspond to rocking modes of the ring CH_2 groups, as well as in the 750 and 800 cm^{-1} to wagging out of plane vibrations involving the carbonyl carbon of EC at lower frequencies and of DMC at higher frequencies. Even in this case, the experimental intensities are markedly higher, as cluster-based simulations cannot fully capture the contributions from the diverse molecular environments present in solution, highlighting the conformational flexibility of the solvent. The band

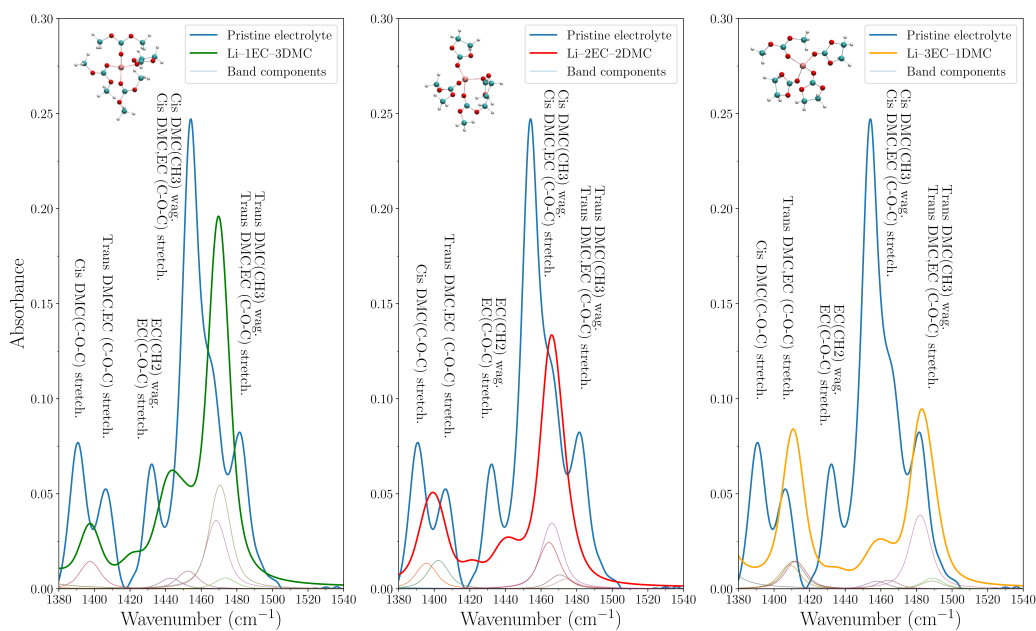


Figure 4.10 IR spectra in the 1380–1540 cm^{-1} region for the pristine electrolyte and Li-1EC-3DMC, Li-2EC-2DMC, and Li-3EC-1DMC clusters. The decomposition into band components highlights the overlap between CH_3/CH_2 wagging modes and asymmetric C–O–C stretching.

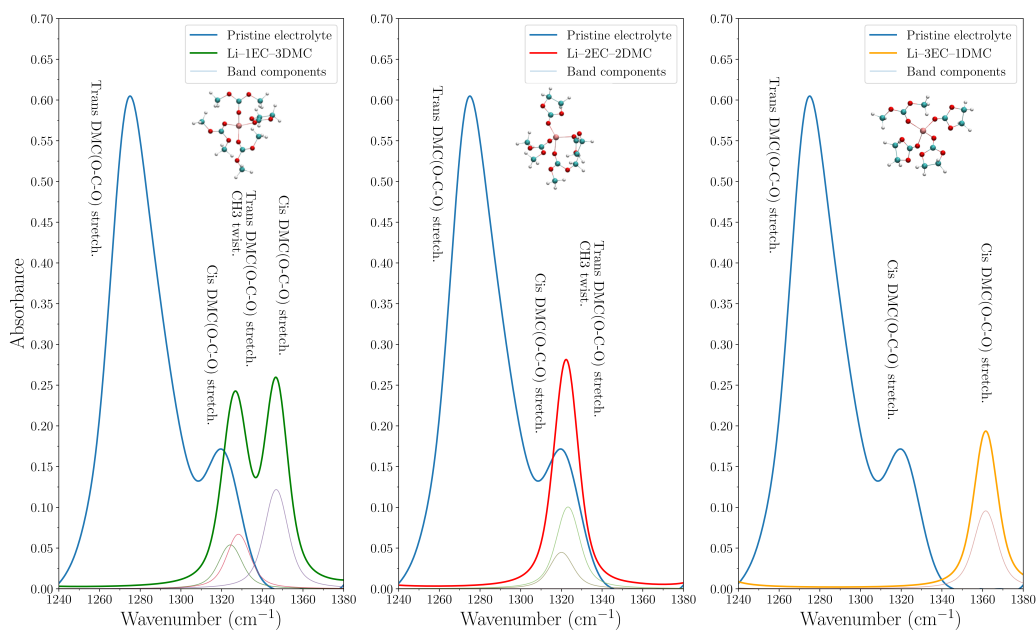


Figure 4.11 IR spectra in the 1240–1380 cm^{-1} region for the pristine electrolyte and Li-1EC-3DMC, Li-2EC-2DMC, and Li-3EC-1DMC clusters. The decomposition into band components highlights the splitting of the asymmetric O–C–O stretching mode into contributions from trans (lower wavenumber) and cis (higher wavenumber) isomers.

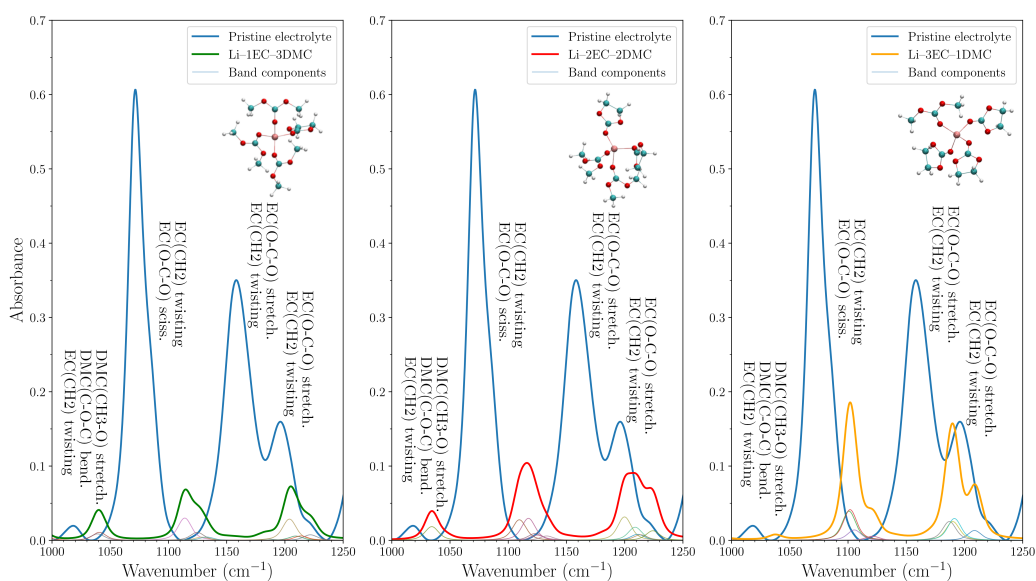


Figure 4.12 IR spectra in the 1000–1240 cm^{-1} region for the pristine electrolyte and Li-1EC-3DMC, Li-2EC-2DMC, and Li-3EC-1DMC clusters. Features include $\text{CH}_3\text{-O}$ stretching of the carbonate backbone, twisting contributions from $-\text{CH}_2$ (EC), and the O-C-O scissoring of EC confined to 1100–1150 cm^{-1} .

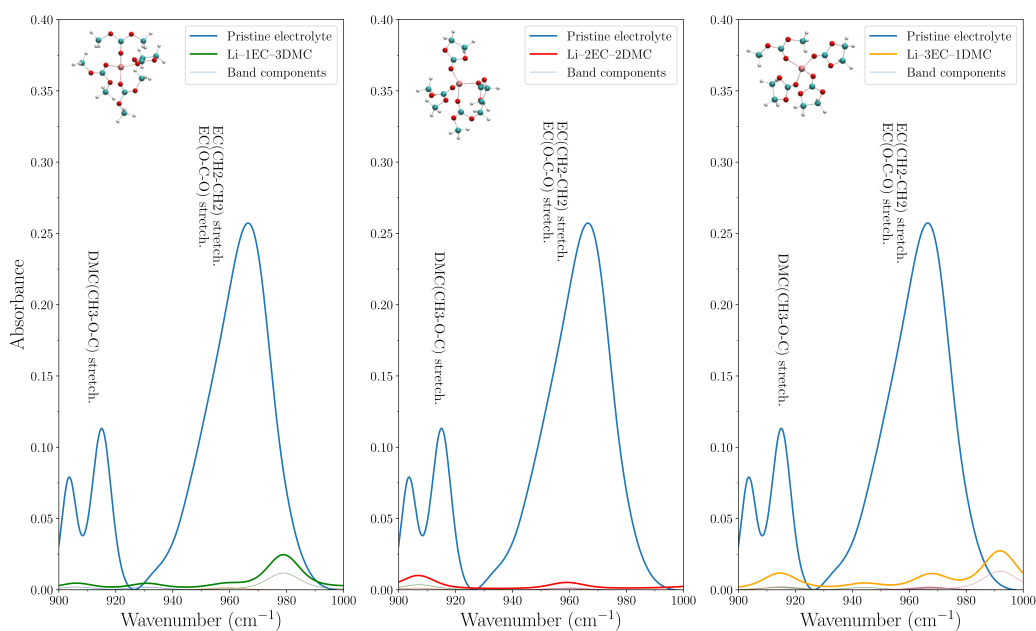


Figure 4.13 IR spectra in the 900–1000 cm^{-1} window for the pristine electrolyte and Li-1EC-3DMC, Li-2EC-2DMC, and Li-3EC-1DMC clusters. The 900–930 cm^{-1} region is mainly associated with $\text{CH}_3\text{-O-C}$ stretching of DMC, while the 930–1000 cm^{-1} region features $\text{CH}_2\text{-CH}_2$ and O-C-O stretching modes of EC.

between 800 and 900 cm^{-1} is assigned to the libration mode of water and is absent

in the simulated spectra, as water molecules are not included in the cluster models. Under ambient conditions, additional contributions appear in the experimental

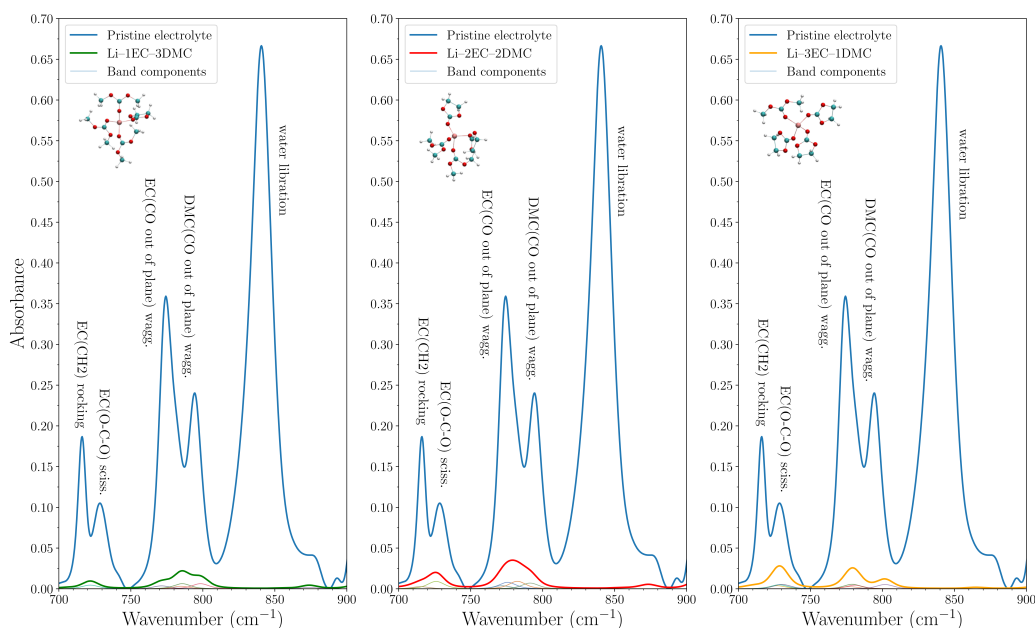


Figure 4.14 IR spectra in the 700–900 cm^{-1} region are shown for the pristine electrolyte and the Li-1EC-3DMC, Li-2EC-2DMC, and Li-3EC-1DMC clusters. Bands between 700–750 cm^{-1} correspond to rocking and scissoring vibrations, while those between 750–800 cm^{-1} are assigned to wagging and deformation modes. The broad feature between 800 and 900 cm^{-1} arises from water libration and is therefore absent in the simulated spectra.

spectra, such as the asymmetric stretching of CO_2 near 2300–2400 cm^{-1} and the bending modes of adsorbed water around 1600 cm^{-1} . These environmental effects, not captured by the cluster simulations, modestly influence the overall spectral shape and contribute to band broadening.

From this analysis, the combined use of experimental infrared spectroscopy and cluster-based DFT simulations enables reliable vibrational band assignments in the LP30 electrolyte, providing detailed insight into the lithium solvation shell structure and molecular interactions within the system. The only unassigned experimental bands are those around 2300–2400 and 1600 cm^{-1} , attributable to CO_2 and residual water.

Additionally, low-frequency bands below 700 cm^{-1} were not clearly assigned to vibrational modes calculated in the clusters, likely because they correspond to collective modes, librations, or motions of larger molecular aggregates not reproducible by isolated cluster models.

In addition, these low-frequency bands may correspond to vibrations of inorganic hydrolysis products such as LiF and phosphate salts. In field-relevant systems, these species are consistently detected as primary outcomes of LiPF_6 degradation, even under mild exposure conditions [114, 115]. The presence of moisture and CO_2 is mechanistically relevant: LiPF_6 is prone to hydrolysis, generating PF_5 , HF , and

subsequently trifluorophosphate (TFP), which can further react to give OPF_2OH and alkoxyfluorophosphates [116, 117]. Such reactions can occur even before electrochemical cycling and contribute to the observed IR background. Moreover, CO_2 evolution is also expected from electrolyte decomposition reactions, e.g. EC reduction and $\text{PF}_5 + \text{Li}_2\text{CO}_3$ chemistry within the SEI [118].

These unassigned signals may therefore arise both from environmental contaminants and from reaction products formed when PF_6^- ions react with ambient moisture and CO_2 , underscoring that the measured spectrum reflects more than the ideal molecular structure of solvents and ions.

Overall, the unassigned IR features in the fresh, air-exposed electrolyte highlight the critical role of ambient interactions: even trace humidity and CO_2 are sufficient to trigger LiPF_6 decomposition chemistry, altering the spectral profile and preconditioning the electrolyte prior to any electrochemical cycling.

To assess the influence of degradation products formed upon ambient exposure, additional clusters were generated in which one of the four Li^+ -coordinated solvent molecules was substituted with either trifluorophosphate (TFP) or diethylene glycol dimethyl ether (DEG–DME), species identified by GC–MS (Section 4.5). For each of the three representative clusters this yielded $3 \times 4 = 12$ configurations per species, resulting in a total of twenty-four modified clusters. Simulated IR spectra of these new clusters reveal significant differences compared to the original clusters, as shown in Figures 4.15 and 4.16.

In the case of TFP substitution (Figure 4.15), new bands emerge in the $920\text{--}1040\text{ cm}^{-1}$ region, associated with P–F bond stretching, and are superimposed on the features observed in Figure 4.13. In addition, other new bands overlap with those shown in Figure 4.10 in the range $1400\text{--}1540\text{ cm}^{-1}$ and correspond to P=O stretching. These spectral features represent clear markers of fluorophosphate-based degradation products, attributable to reactions occurring upon exposure to the ambient atmosphere, and notably, they are also observed in the spectrum of the pure electrolyte that was exposed to air during the measurement. Specifically, in the Li-3EC-1DMC cluster substituted with TFP, these bands are prominent alongside reductions and shifts in the carbonyl (C=O) stretching bands of EC and DMC, indicating modifications in lithium coordination. Low-frequency modes between $800\text{--}900\text{ cm}^{-1}$ exhibit additional low-intensity contributions from phosphate-related torsional and bending vibrations, confirming changes in the solvation environment. These bands add to the contribution associated with the libration mode of water shown in Figure 4.14. Similarly, the Li-2EC-2DMC cluster with TFP substitution exhibits phosphate-related and P–F vibrational bands in the $920\text{--}1040\text{ cm}^{-1}$ region. Furthermore perturbations in the carbonyl region and new low-frequency modes support altered lithium coordination.

The Li-1EC-3DMC cluster also displays analogous spectral modifications upon TFP substitution, confirming the impact of degradation through phosphate-associated bands and carbonyl vibration shifts.

In addition, the characteristic band in the range $1600\text{--}2000\text{ cm}^{-1}$, in the simulated spectras, undergoes a more pronounced splitting, which is indicative of changes in the solvation environment. This splitting, however, was not observed in the experimental spectrum of the pristine electrolyte.

These observations indicate that the formation of phosphate-related bands requires

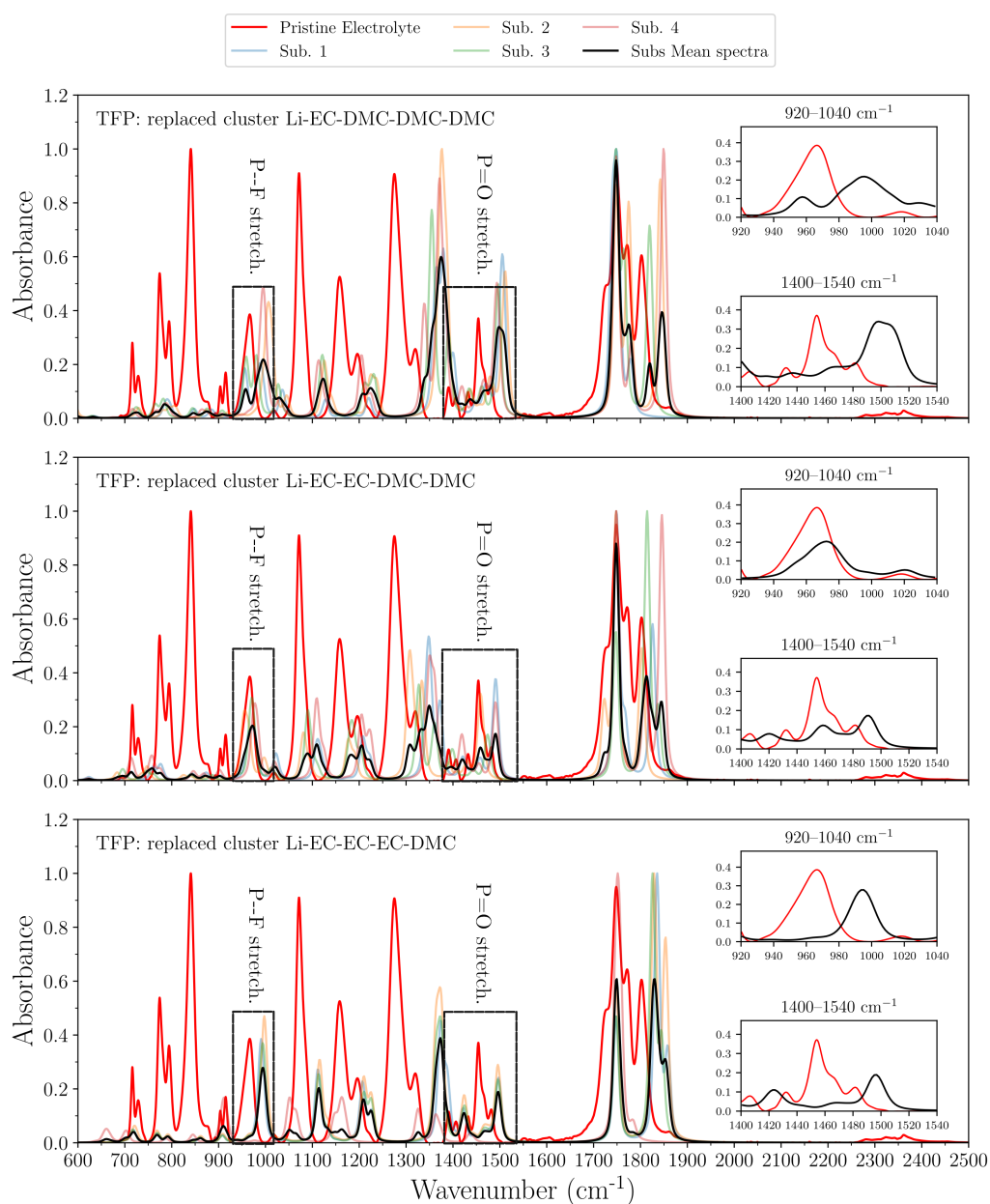


Figure 4.15 Simulated IR spectra of lithium solvation clusters obtained by substituting each coordinating solvent molecule individually with trifluorophosphate (TFP). The spectra correspond to different substitution sites within the clusters of compositions Li-EC-DMC-DMC-DMC, Li-EC-EC-DMC-DMC, and Li-EC-EC-EC-DMC.

complex degradation processes and can involve both environmental exposure and reactions with atmospheric moisture.

For DEG-DME substituted clusters (Figure 4.16), new bands emerge prominently in the 1100-1250 cm^{-1} region, corresponding to C–O and C–C stretching vibrations characteristic of DEG-DME functional groups. These features are consistent with the spectral signatures observed in the electrolyte upon exposure to the ambient

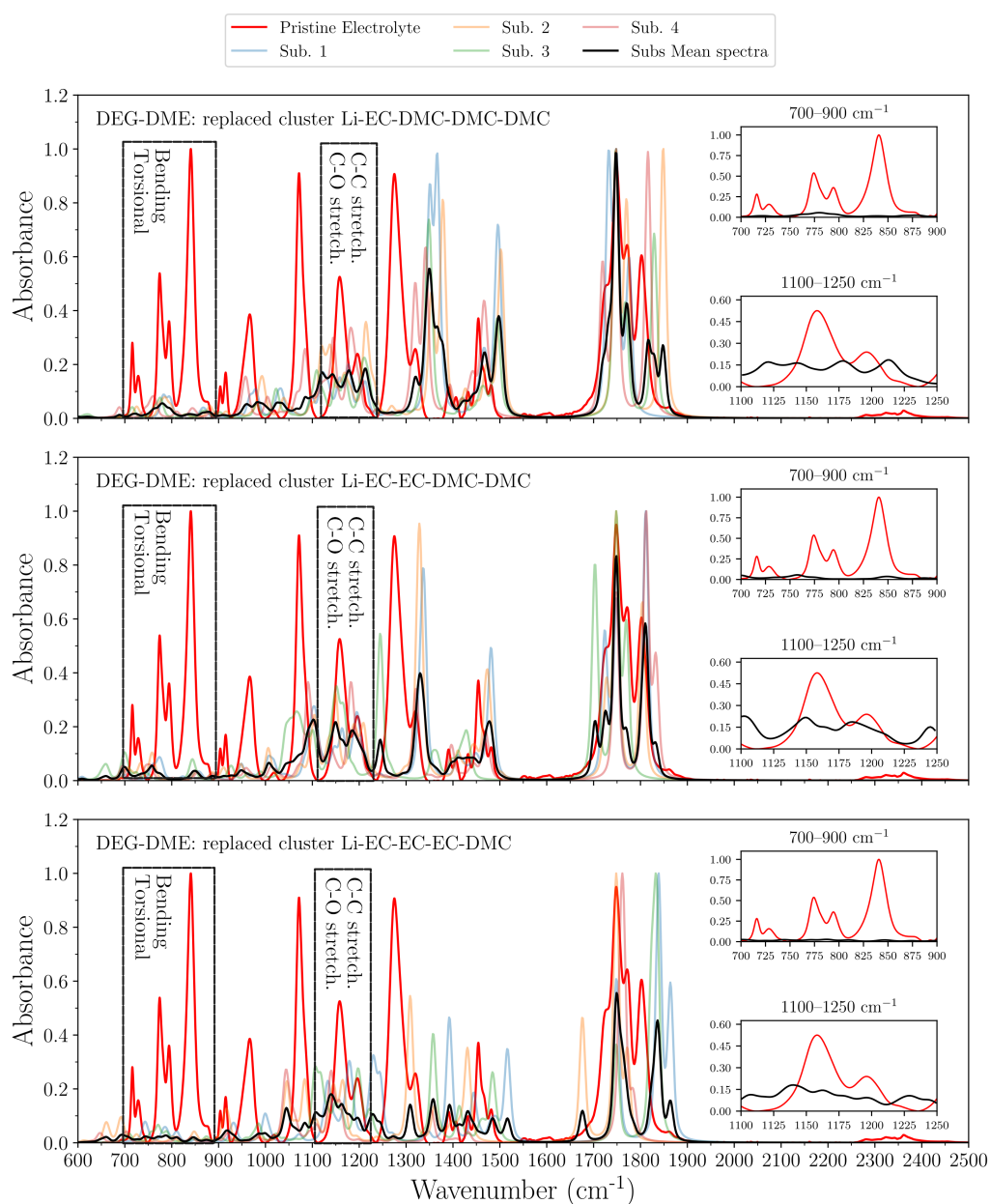


Figure 4.16 Simulated IR spectra of lithium solvation clusters obtained by substituting each coordinating solvent molecule individually with diethylene-glycol dimethylether (DEG-DME). The spectra correspond to different substitution sites within the clusters of compositions Li-EC-DMC-DMC-DMC, Li-EC-EC-DMC-DMC, and Li-EC-EC-EC-DMC.

atmosphere, confirming the incorporation of ether- or glycol-based degradation products into the lithium solvation shell.

Across all DEG-DME substituted clusters, carbonyl (C=O) stretching bands of EC and DMC exhibit shifts and intensity variations, reflecting altered lithium coordination. Additional low-frequency modes, in the range 700–900 cm^{-1} , show increased contributions from torsional and bending vibrations related to DEG-DME molecular

motions, confirming the impact on solvation structure and overlap with the bands in Figure 4.14.

Overall, these results underscore the importance of including degradation products such as TFP and DEG-DME in spectral interpretations to comprehensively understand electrolyte aging and environmental effects on lithium solvation shells.

At this stage, to identify potential contributions arising from the procedure of opening the cells during recycling, the same comparison performed for the pristine electrolyte was conducted using the IR spectrum collected from a set of three cells that were only closed and opened, hence not cycled. This comparison is presented in Figure 4.17. Analysis of the experimental IR spectra from non-cycled cells, in

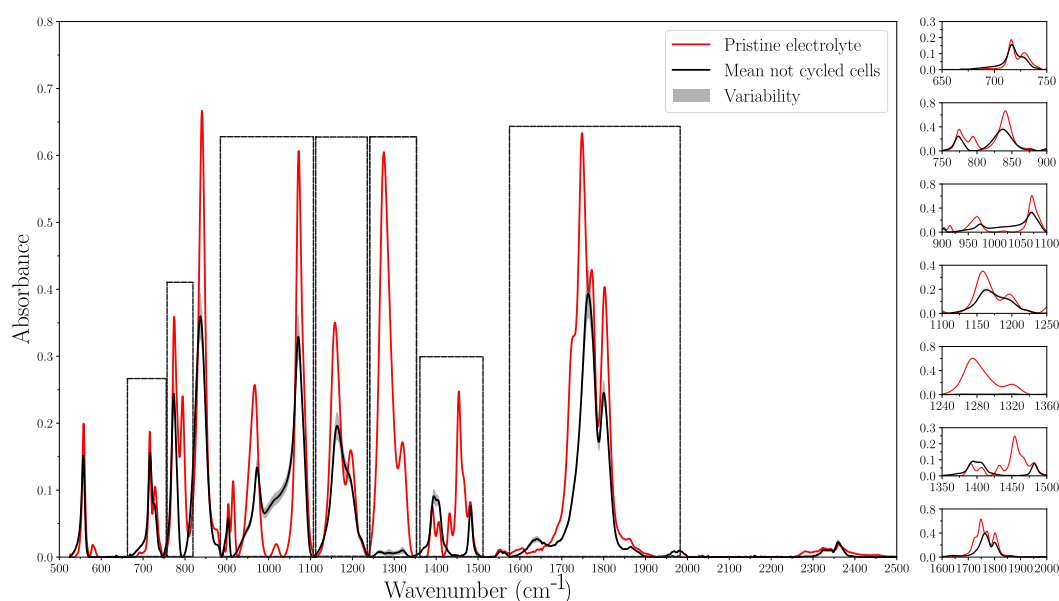


Figure 4.17 Comparison between the IR spectrum of the pristine electrolyte (red) and the average spectrum of the opened and closed but not-cycled cells (black), with the associated variability indicated in light gray. On the right: magnified views of seven identified regions: 680–750, 750–810, 900–1100, 1100–1250, 1240–1350, 1420–1500, and 1600–2000 cm^{-1} .

comparison with the pristine electrolyte spectrum, reveals a pronounced attenuation or, in several cases, the disappearance of specific features. In the 680–750 cm^{-1} region, the secondary component of the band, associated to EC O–C–O scissoring (Figure 4.14) decreases. Between 750 and 810 cm^{-1} , the out of plane contribution previously observed is no longer discernible and is more appropriately assigned to a methyl rocking/wagging mode or to a deformation of the $\text{CH}_3\text{--O--C}$ moiety of DMC or other ether/glycol-derived species, rather than to a $\text{CH}_2\text{--O--C}$ mode of EC. In the 900–1100 cm^{-1} region, the intensity of the bands previously attributed to P–F stretching, as well as to solvent-related modes described in Figure 4.12, decreases, while the features assigned to C–O–C bending and $\text{CH}_3\text{--O}$ stretching of DMC become more pronounced. Moving to 1100–1240 cm^{-1} (Figure 4.12), the EC O–C–O stretching band further weakens; at higher frequencies, a particularly marked attenuation is observed in the 1240–1350 cm^{-1} region, associated with the O–C–O stretching of DMC (Figure 4.11). Between 1420 and 1500 cm^{-1} , features

associated with cis-DMC and with EC decrease, leaving predominantly trans-DMC signatures. Finally, in the characteristic 1600–2000 cm^{-1} window (Figure 4.9), the DMC-related bands converge (reduced splitting), while the position of the EC band remains essentially unchanged. Overall intensities are reduced across the spectrum. As summarized in Table 4.1, the spectral changes observed in the not-cycled cell compared to the pristine electrolyte affect several frequency regions. This observation

Wavenumber region (cm^{-1})	Main assignments (pristine electrolyte)	Observed changes in non-cycled cell	Interpretation / Remarks
680–750	EC O–C–O scissoring (secondary component)	Band intensity decreases	Partial loss of EC-related coordination environment
750–810	Out-of-plane CH_2 –O–C mode of EC	Feature no longer discernible; attributed to CH_3 rocking/wagging or CH_3 –O–C deformation of DMC / ether–glycol species	Reduction of EC contribution; emergence of ether-derived species
900–1100	P–F stretching and solvent-related modes; DMC C–O–C bending and CH_3 –O stretching	P–F and solvent-mode intensities decrease; DMC-related features become more pronounced	Possible partial salt decomposition; increased relative DMC contribution
1100–1240	EC O–C–O stretching	Further weakening of the EC band	Progressive depletion of EC-related species
1240–1350	DMC O–C–O stretching	Marked attenuation	Structural modification or loss of DMC
1420–1500	cis-/trans-DMC and EC vibrations	cis-DMC and EC features decrease; trans-DMC signatures predominate	Conformational rearrangement within DMC molecules
1600–2000	DMC and EC characteristic stretching modes	DMC bands converge (reduced splitting); EC band position unchanged; overall intensity reduced	Solvent reorganization and loss of distinct DMC conformers

Table 4.1 Summary of FT-IR wavenumber regions, pristine electrolyte assignments, and observed changes in the non-cycled cell.

suggests that significant chemical modifications or alterations of the local molecular environment may occur during the recycling process. These alterations are likely driven by exposure to ambient conditions during cell opening and handling, resulting in partial degradation or reorganization of the electrolyte components, and may be further promoted by the intrinsic volatility of DMC.

To elucidate the origin of these spectral variations, a direct comparison was undertaken with simulated IR spectra of lithium solvation clusters incorporating degradation products, previously identified through GC–MS analysis.

These substituted clusters exhibit modifications in the vibrational modes, which correspond well to the reduced bands observed experimentally in the non-cycled cells. In particular, the phosphate- and P–F-related vibrations from TFP and the

C–O and C–C stretching modes from DEG-DME provide plausible explanations for the changes in spectral intensity and band disappearance.

Figures 4.18 and 4.19 illustrate the comparison between the simulated spectra of TFP- and DEG-DME-substituted clusters and the average experimental spectrum of the non-cycled cells. The good agreement supports the hypothesis that environmental exposure leads to chemical alterations, reflected by the diminished intensity or loss of characteristic bands before any cycling-induced aging.

This analysis highlights the need to account for environmental and procedural influences when interpreting electrolyte spectra and during recycling, since such factors can induce changes independent of electrochemical reactions and significantly alter the spectral fingerprint of the electrolyte system.

A detailed analysis shows that in the 1400–1480 cm^{-1} region, the first two peaks of the bands observed in the pristine electrolyte (Figure 4.10) disappear in the non-cycled cells, and the corresponding vibrational modes characteristic of phosphate groups no longer find a direct counterpart.

This suggests that the phosphate group ($\text{F}_3\text{P}=\text{O}$) in the TFP degradation product has opened, with the phosphoryl oxygen forming an additional bond, resulting in a pentacoordinated phosphorus center ($-\text{F}_3\text{P}-\text{O}-$). On the other hand, the band related to P–F stretching in the 900–1000 cm^{-1} region remains visible. These vibrations confirm the presence of phosphate-related bands, likely arising from environmental exposure and handling of the cells. In addition this spectral window, the band between 1000 and 1040 cm^{-1} , associated with C–O–C bending motions and $\text{CH}_3\text{--O}$ stretching of DMC (Figure 4.12), increases in intensity, indicating the formation of ether/glycol-derived species in the system.

In the 1000–1250 cm^{-1} region, bands associated with C–O and C–C stretching typical of DEG-DME are present in both the DEG-DME substituted clusters and the spectrum of the non-cycled cells, indicating a significant impact of organic degradation products on the lithium solvation structure.

Moreover, the carbonyl ($\text{C}=\text{O}$) bands between 1750 and 1800 cm^{-1} exhibit shifts and intensity variations consistent with modifications in the lithium coordination environment due to these degradation species.

Finally, enhanced, low intensity, torsional and bending modes are observed in the low-frequency region (700–900 cm^{-1}), reflecting the introduction of new molecular species in the substituted clusters and mirroring structural changes induced by degradation.

These findings indicate that the new bands detected in the opened and closed but non-cycled cells can be assigned to specific degradation products identified through cluster-based IR simulations, highlighting the importance of considering environmental and procedural effects in the spectroscopic characterization and recycle process of battery electrolytes.

Having identified the species with their respective vibrational modes contributing to the relevant IR bands, and having distinguished the contributions arising from moisture exposure and the recycling process, it became possible to compare the spectrum of closed but non-cycled cells with those of electrolytes at various aging stages obtained through the different protocols described in Section 4.4. From this comparison, three distinct new IR bands were identified for each of the six electrolyte aging conditions and compared against the reference spectrum obtained

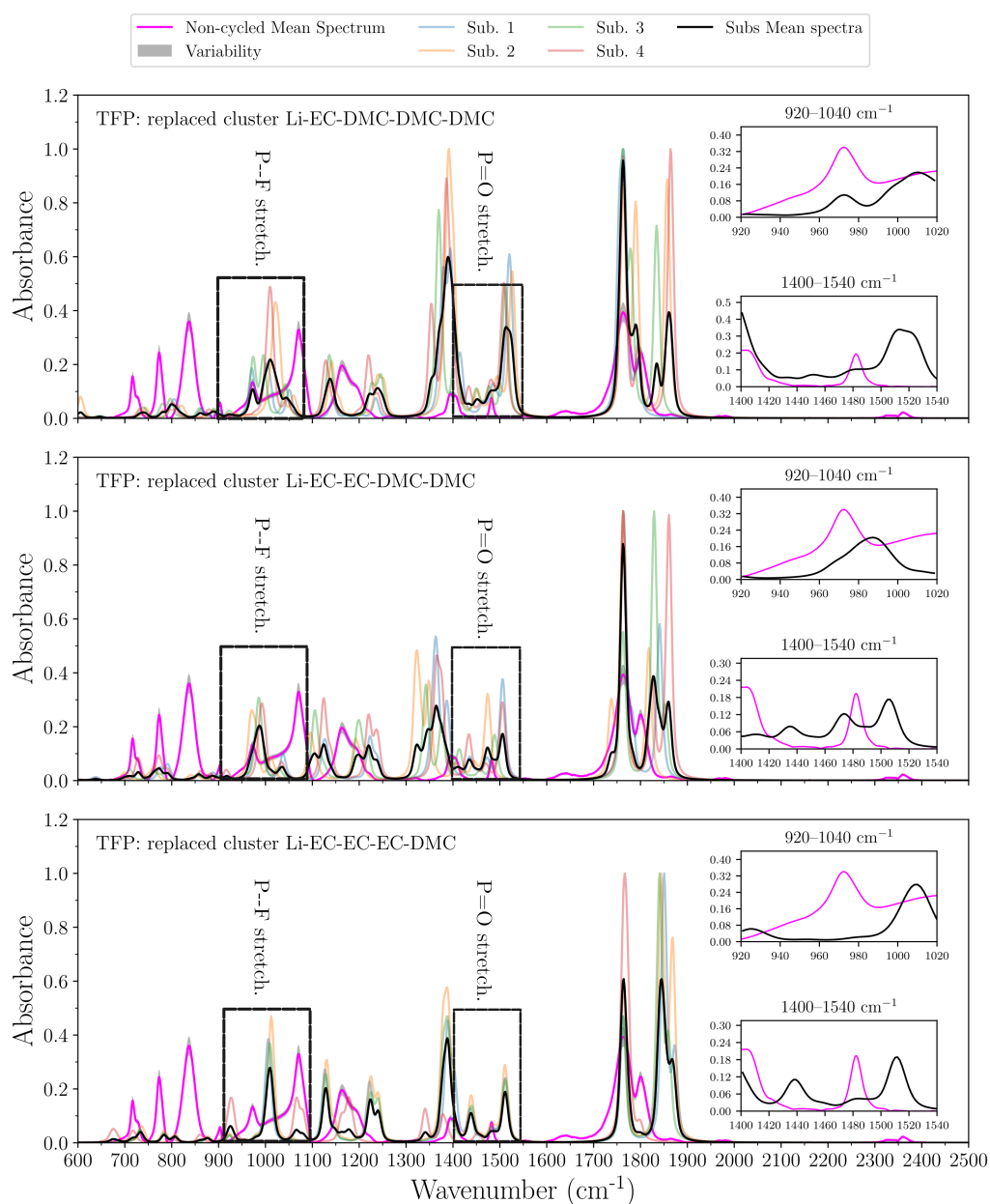


Figure 4.18 Comparison of simulated IR spectra for lithium solvation clusters substituted with trifluorophosphate (TFP) and the average spectrum of the opened and closed but non-cycled cells. The different spectra Sub. 1–4 correspond to substitution of each coordinating molecule with TFP in clusters composed of Li-EC-DMC-DMC-DMC, Li-EC-EC-DMC-DMC, and Li-EC-EC-EC-DMC. Phosphate-related degradation bands are highlighted.

as the average of the non-cycled cells. The first new band emerged in the region between 1225 and 1350 cm^{-1} , the second between 1425 and 1500 cm^{-1} , and finally the third within 1900 to 2400 cm^{-1} .

Detailed examination of the spectral region between 1225 and 1350 cm^{-1} (Figure

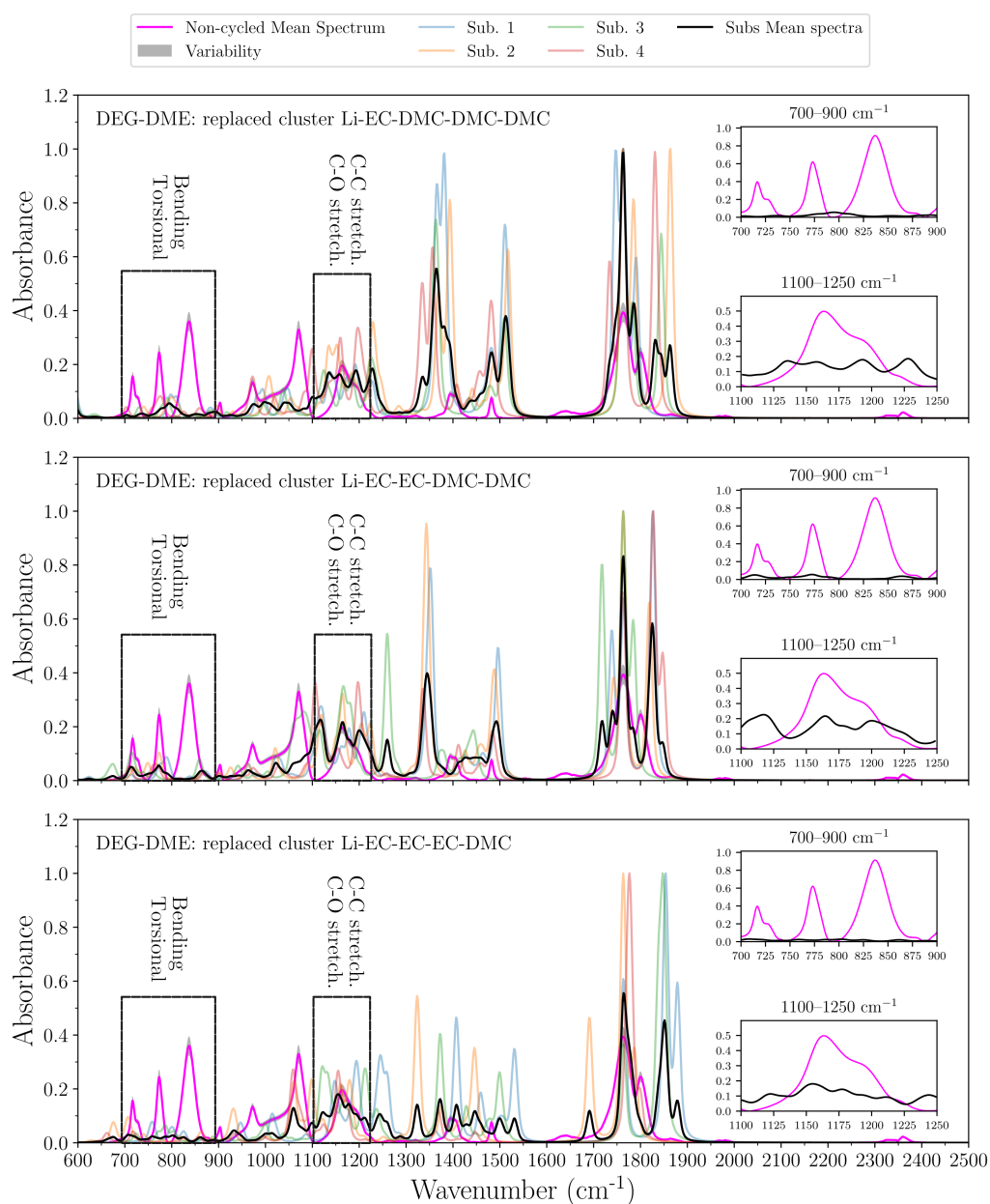


Figure 4.19 Comparison of simulated IR spectra for lithium solvation clusters substituted with diethylene glycol dimethyl ether (DEG-DME) and the average spectrum of the opened and closed but non-cycled cells. The different spectra Sub. 1–4 correspond to substitution of each coordinating molecule with DEG-DME in clusters composed of Li-EC-DMC-DMC-DMC, Li-EC-EC-DMC-DMC, and Li-EC-EC-EC-DMC. Ether/glycol-derived vibrational contributions are highlighted.

4.20) reveals a clear growth and appearance of new bands associated with O–C–O stretching modes and phosphate-related vibrations. These features are consistent with the formation of degradation species such as TFP, carbonyl-containing compounds, and DEG-DME, as supported by cluster-based IR simulations.

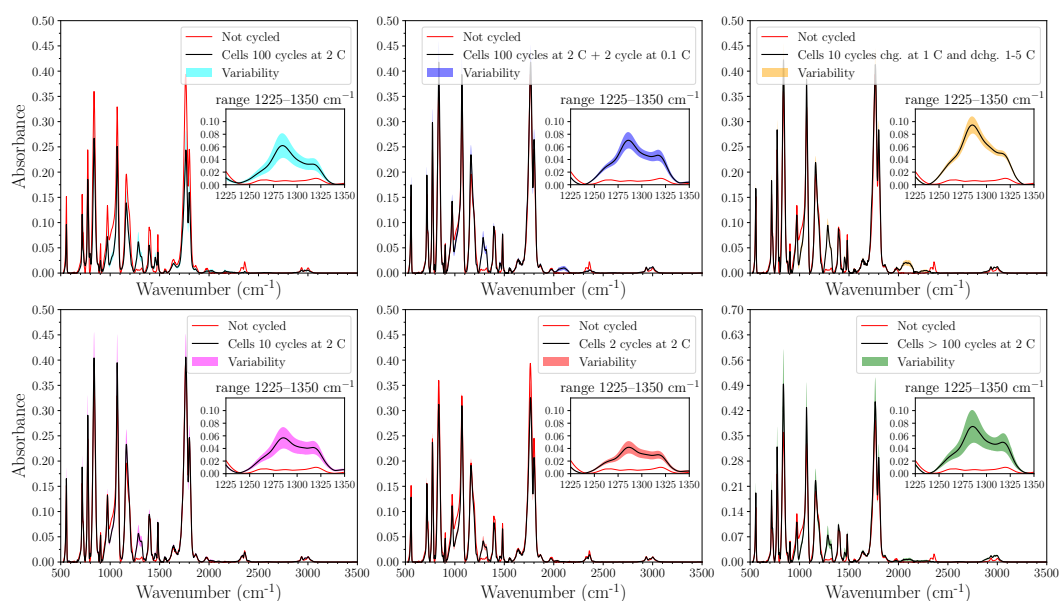


Figure 4.20 Zoom on the 1225–1350 cm^{-1} region illustrating the growth and appearance of new bands associated with O–C–O stretching modes and phosphate-related vibrations. These spectral changes are consistent with degradation involving TFP, carbonyl-containing compounds, and DEG-DME species.

In the 1425–1500 cm^{-1} range (Figure 4.21), an increase in intensity is observed around 1460 and 1495 cm^{-1} .

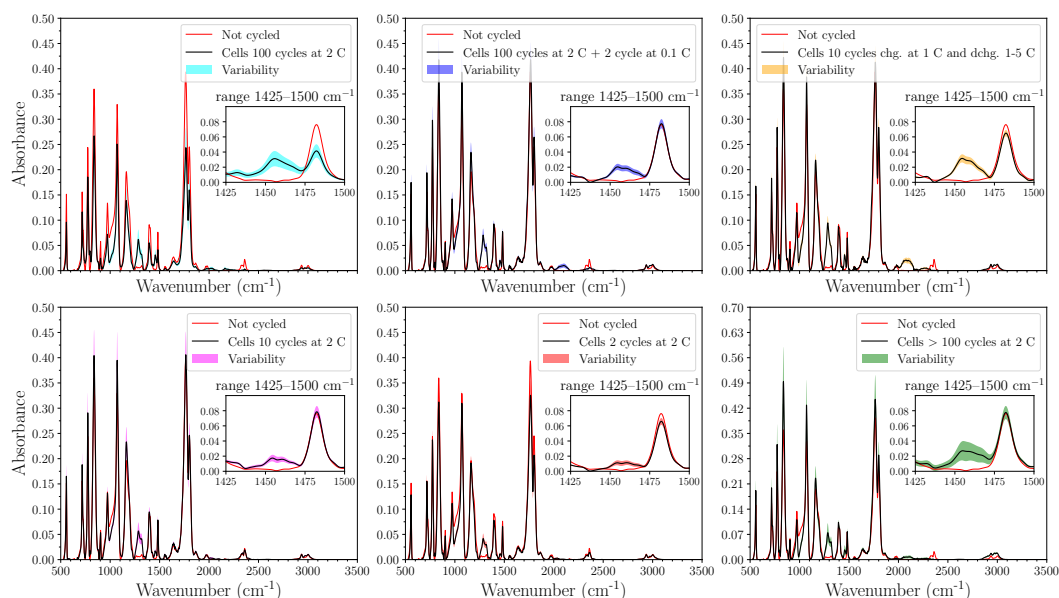


Figure 4.21 Zoom on the 1425–1500 cm^{-1} region showing an intensity increase around 1495 cm^{-1} with aging. This band corresponds to wagging modes of $-\text{CH}_3$ groups primarily from DMC and is enhanced by phosphate-related (TFP) and ether/glycol-derived (DEG–DME) degradation products.

The new band emerging near 1460 cm^{-1} is assigned to C–O–C stretching combined with $-\text{CH}_3$ wagging, indicating the formation of new glycol- or ether-like species and an increase in terminal methyl groups. On the other hand, the band near 1490 cm^{-1} overlaps well with the reference spectrum and is primarily attributed to C–O–C stretching modes together with vibrational modes of methyl (CH_3) and methylene (CH_2) groups, predominantly originating from DMC or EC solvent molecules within the lithium solvation shell. This observation suggests that, given the higher volatility and reactivity of DMC, the formation of ether- or glycol-like compounds is favored, which preferentially adopt trans conformations of oxygen-bonded groups. This assignment is further supported by DFT IR simulations performed on representative Li–EC–DMC clusters, where vibrational modes in this region exhibit characteristic angular deformations of aliphatic groups.

Additionally, simulations on lithium solvation clusters substituted with, GC-MS identified, degradation products, reveal further contributions in the $1400\text{--}1500\text{ cm}^{-1}$ range. In TFP-substituted clusters, vibrational modes associated with phosphate groups and P–F bonds overlap in this spectral region, while DEG–DME-substituted clusters contribute vibrational modes from ether and alkyl chain bending and stretching. Consequently, the intensity and precise position of the band near 1460 cm^{-1} in experimental spectra of aged electrolytes reflect a convolution of vibrational contributions from both the original solvent molecules and degradation, glycol or ether based, products formed during cycling.

The band at 1495 cm^{-1} is attributed primarily to wagging modes of methyl groups from DMC, whose presence is amplified by degradation products including TFP and DEG–DME derivatives formed during aging and environmental exposure. Finally, the $1900\text{ to }2400\text{ cm}^{-1}$ spectral window (Figure 4.22) highlights the emergence of a weak new broad band near $1925\text{--}2100\text{ cm}^{-1}$ in aged electrolytes, absent in pristine and non-cycled samples. This band is assigned to oxidative degradation products, further confirming the impact of environmental exposure and electrochemical cycling on electrolyte composition.

In summary, the infrared spectra of aged electrolytes reveal new vibrational bands that cannot be explained by pristine solvent molecules and LiPF_6 alone. Cluster simulations including TFP and DEG–DME reproduce these features, confirming that degradation products are incorporated into the lithium solvation shell and actively shape its structure. Importantly, several of these bands are also observed in spectra from cells that were opened but not cycled, demonstrating that environmental exposure and handling during recycling already contribute to measurable changes in electrolyte composition. Electrochemical cycling then amplifies or reshapes this altered baseline, resulting in the convolution of cycling-induced modifications with environmental effects.

These findings emphasize that a complete interpretation of electrolyte infrared spectra, collected at ambient atmosphere, must account not only for the pristine molecular components, but also for degradation products and ambient interactions. This broader perspective is essential for understanding electrolyte stability in lithium-ion batteries recycle. Moreover, it highlights that the recycling process itself can influence the recovered electrolyte chemistry, with direct consequences for both the accuracy of spectroscopic analysis and the overall efficiency of recycling strategies.

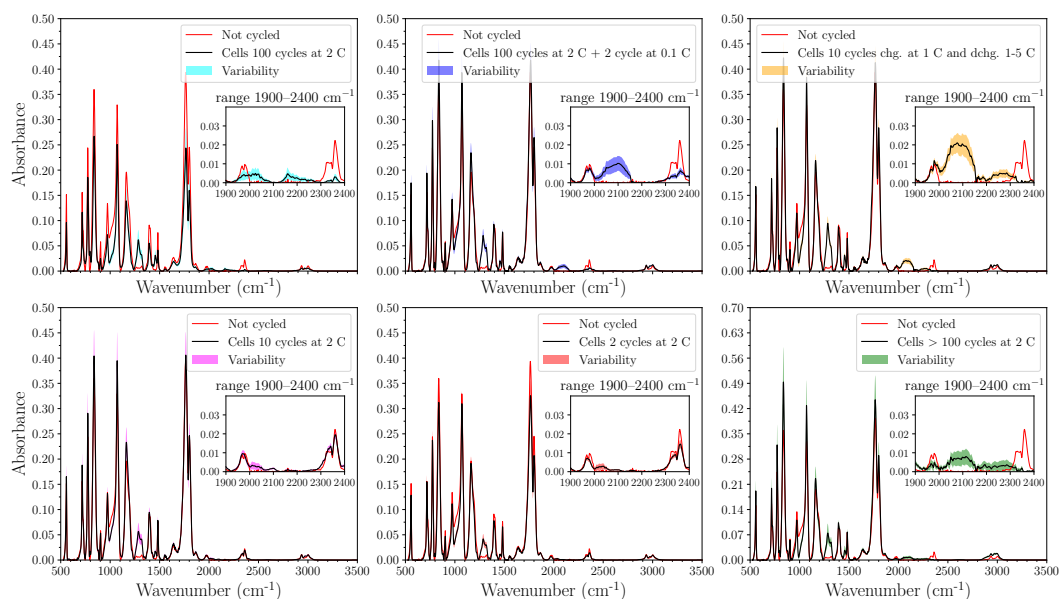


Figure 4.22 Zoom on the 1900–2400 cm^{-1} region highlighting the emergence of a new weak band near 1925 cm^{-1} in aged electrolytes compared to pristine and non-cycled samples. This band is attributed to oxidative degradation products, including phosphate-related (TFP) and ether/glycol-derived (DEG–DME) species.

4.7 Concluding Remarks and Future Directions

In this chapter, a comprehensive methodology for the recovery, recycling, and analysis of electrolytes from spent LiFePO_4 (LFP) batteries has been presented. The experimental workflow included (i) the safe disassembly of spent SNAM pouch cells, (ii) recovery and reprocessing of LFP/FP powders, (iii) fabrication and electrochemical cycling of coin half-cells, and (iv) molecular-level characterization of electrolyte aging using GC–MS and FT-IR spectroscopy supported by molecular dynamics and quantum chemical simulations.

The electrochemical results demonstrated that, although the absolute capacities of recycled LFP electrodes remain lower than those of pristine systems, the protocols allowed reliable evaluation of electrolyte degradation mechanisms. Cycling at high C-rates accelerated capacity fading and polarization growth, in line with electrolyte decomposition and interfacial instability. Complementary GC–MS data confirmed an average $A(\text{DMC})/A(\text{EC})$ ratio of about 0.5 across aging conditions, reflecting not only the higher volatility of dimethyl carbonate but also its greater consumption during cycling. Thus, DMC is depleted roughly twice as fast as ethylene carbonate, although both solvents exhibit comparable relative trends over extended cycling. This underscores the combined influence of volatility and reactivity on electrolyte stability and highlights the importance of maintaining solvent balance to ensure long-term performance and to facilitate safe cell recycling. In parallel, FT-IR spectroscopy revealed the emergence of new vibrational features attributable to phosphate-related species such as trifluorophosphate (TFP) and to ether/glycol-derived species such as diethylene glycol dimethyl ether (DEG–DME). These species were consistently assigned through cluster-based DFT simulations, highlighting the interplay between

electrochemical stress and environmental exposure during recycling.

Overall, the combined experimental and computational approach provided a consistent picture of electrolyte aging pathways, emphasizing the dual role of cycling protocols and ambient atmosphere in shaping electrolyte stability and its composition for the recycle. The results also point out that cell opening and handling during recycling may trigger early degradation reactions, thereby affecting both the efficiency and the quality of recovered electrolyte.

Future developments should focus on: (i) refining recycling protocols to minimize environmental exposure during cell disassembly, (ii) extending molecular simulations to explicitly include hydrolysis and CO₂-driven reactions, and (iii) exploring alternative, more stable electrolyte formulations to enhance the reusability of recovered components.

By bridging electrochemical performance with molecular-scale insights, this work contributes to establishing a framework for the sustainable recycling of lithium-ion batteries.

Chapter 5

Conclusions

This thesis has pursued two complementary objectives: to develop advanced methods for designing and characterizing calcium-based electrolytes, and to investigate the chemical evolution of LFP batteries LP30 electrolyte subjected to different degrees of aging. These two lines of inquiry are linked by a shared methodological framework that combines molecular simulations and spectroscopic analysis, offering insights that are relevant both to the exploration of new battery chemistries and to the sustainable management of existing ones.

From a methodological standpoint, the work integrates classical and polarizable molecular dynamics and DFT-based vibrational calculations with experimental Raman and FT-IR spectroscopy, establishing a coherent approach to identify solvation motifs and their spectral signatures. This computational–experimental interplay enhanced the reliability of structural assignments and allowed vibrational spectra to be interpreted with greater confidence. On the experimental side, the thesis refined the use of Raman and FT-IR spectroscopy for electrolyte characterization and complemented the FT-IR spectroscopy technique with GC–MS analysis in the study of aged LP30 electrolyte. The result is a reproducible framework for probing both model electrolytes and chemically complex, real-world samples.

The investigation of $\text{Ca}(\text{TFSI})_2$ in propylene carbonate provided new understanding of its solvation behavior. The results reveal a clear dependence of coordination structure on concentration: calcium is primarily solvent-coordinated at lower salt contents, while the role of TFSI anions becomes increasingly important at higher concentrations. Crucially, the study identified an intermediate concentration range of about 0.5–0.6 M where the fraction of solvent-coordinated calcium is maximized, and the relative contribution of TFSI coordination, though still evident, is comparatively reduced. This regime corresponds to the condition in which the solution contains the highest proportion of free calcium ions not bound to the anion, and for this reason it represents an optimal concentration window. Its spectroscopic fingerprint can thus serve as a practical reference for the design of calcium-ion electrolytes.

In parallel, the analysis of LP30 electrolytes recovered from LiFePO_4 cells at different aging states revealed that even partially aged electrolytes exhibit chemical modifications compared to pristine solutions. Infrared spectra revealed the appearance and growth of bands attributable to degradation products, particularly fluorophosphate species derived from LiPF_6 , which can undergo further reactions leading to ether- or

glycol-derived compounds such as DEG-DME; these assignments were corroborated by GC-MS measurements. These results demonstrate that electrolyte aging is a progressive process, marked by the gradual accumulation of decomposition products whose presence can be monitored through spectroscopic markers. By identifying and assigning these features, the thesis contributes tools for assessing the chemical state of aged electrolytes and for supporting decisions about their possible purification and reuse.

Taken together, these findings show how the combination of predictive computation and spectroscopy-driven experimentation can illuminate both the design of new calcium-based electrolytes and the diagnosis of aging processes in lithium-based systems. The identification of an optimal concentration regime in $\text{Ca}(\text{TFSI})_2/\text{PC}$ and the characterization of aging signatures in LP30 highlight the scientific and practical value of the methodological advances developed here.

Looking ahead, further refinement of polarizable force fields and expanded sampling strategies will improve the description of coordination equilibria in calcium systems. Operando spectroscopic studies would enable direct correlation of solvation changes with electrochemical performance. For lithium-ion electrolyte recycling, systematic studies linking the nature of impurities to electrochemical outcomes will be crucial to transform diagnostic tools into actionable industrial practices.

By advancing methodology and applying it to both novel and aged electrolytes, this thesis contributes to the rational design of calcium-ion systems and to the development of diagnostic tools for monitoring the evolution of commercial lithium-ion electrolytes, thereby reinforcing the connection between electrolyte innovation and long-term sustainability in energy storage.

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