

Facile SEI Improvement in the Artificial Graphite/LFP Li-ion System: via NaPF_6 and KPF_6

Electrolyte Additives

by

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

Lithium-ion batteries (LIBs) are the most widely used energy storage technologies for grid-scale applications, electric cars, and portable devices because of their consistent voltage profiles, high energy density, and extended cycle life. However, interfacial degradation events, especially at the anode, frequently restrict their long-term performance. The creation of the solid electrolyte interphase (SEI) layer, a passivation film that occurs on the graphite anode surface during the initial cycles, is one of the most important issues in this context. Increased impedance, irreversible capacity loss, and decreased coulombic efficiency are caused by unstable or excessive SEI production, which is necessary for stabilizing the electrode–electrolyte interface. These issues are made worse by fast charging or prolonged cycling.

This thesis uses artificial graphite anodes and lithium iron phosphate (LFP) cathodes to examine the effects of sodium hexafluorophosphate (NaPF_6) and potassium hexafluorophosphate (KPF_6) additives on SEI properties and electrochemical performance in LIBs. These alkali salt additives, which are rarely investigated in lithium-ion systems, are being investigated as scalable and affordable substitutes for traditional SEI-modifying additives. The effects of the additives were evaluated by electrochemical testing, which included galvanostatic cycling, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS), as well as surface and structural characterization (SEM and XPS).

According to our results, using KPF_6 and NaPF_6 considerably lowers irreversible capacity loss (by 38.98% and 37.85%, respectively) as compared to a baseline LiPF_6 electrolyte. Additionally, full cell tests show enhanced capacity retention without adversely altering ionic conductivity, with 67.39% for NaPF_6 and 30.43% for KPF_6 across 20 cycles. High-conductivity electrodes used for SEI generation at 1C further validated the additives' capacity to continue functioning during faster formation. These

results provide new perspectives on mixed-ion SEI engineering and show how promising NaPF₆ and KPF₆ are for improving LIB performance in demanding applications like electric vehicles.

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Lastly, I want to express my gratitude to Dr. Pope for kindly letting me use his lab and equipment, which were crucial to finishing my research.

Dedication

This thesis is dedicated to my parents, my brother, and his wife, Yulia. I could not have completed this journey without their unwavering love and support. The sacrifices they made to help me get here mean the world to me, and I will always be grateful for their constant encouragement, understanding, and belief in me.

I also dedicate this work to the memory of my uncle, who passed away this year. Not a day goes by that I don't think about him. I still feel his presence and guidance, and his influence continues to inspire me through every step of this journey.

To all of them, I owe more than words can ever express. This achievement is as much theirs as it is mine.

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List of Abbreviations

LIBs	Lithium-ion Batteries
SEI	Solid Electrolyte Interphase
LFP	Lithium Iron Phosphate
NMC	Nickel Manganese Cobalt
CE	Coulombic Efficiency
CV	Cyclic Voltammetry
EIS	Electrochemical Impedance Spectroscopy
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
GCD	Galvanostatic Charge-Discharge
FEC	Fluoroethylene Carbonate
VC	Vinylene Carbonate
LiBOB	Lithium bis(oxalate)borate
NaPF ₆	Sodium Hexafluorophosphate
KPF ₆	Potassium Hexafluorophosphate
LiPF ₆	Lithium Hexafluorophosphate
BEV	Battery Electric Vehicle
ICEV	Internal combustion Engine Vehicle
R _s	Solution Resistance
R _{ct}	Charge Transfer Resistance
W	Warburg Impedance
CPE	Constant Phase Element
OCV	Open Circuit Voltage

Chapter 1

Introduction

1.1 Lithium-Ion Batteries: An Overview

Since its introduction in 1991, lithium-ion batteries (LIBs) have seen significant development as a source of power for portable electronics, especially laptop computers and cell phones. Large-scale power sources and energy storage devices, such as electric vehicle and renewable energy systems, are now part of LIBs' growing application spectrum[1]. High discharge power, long service life, and high energy density are characteristics of lithium-ion batteries (LIBs). These traits enabled the proliferation of information technology devices across society and a notable advancement in portable electronics technology. With their growing use in large-scale storage systems and electric cars, they offer a viable way to address resource conservation and environmental preservation issues[2]. As a result of increased interest in both academia and industry, energy and power density have steadily improved, and costs have dropped even more quickly. Important considerations, however, are how to achieve the desired outcome of sustainable energy storage and how much and how quickly performance may be further enhanced. These days, lithium-ion batteries are the preferred technology for almost all applications, even though other technologies, including sodium-ion batteries, have been the subject of much research and may have benefits [3], [4]. Thus, their applications can be significantly expanded and new energy storage-dependent technologies made possible by enhancing their performance[5].

The reversible flow of lithium ions via an electrolyte between the cathode and anode during charge and discharge is essential to the operation of lithium-ion batteries. Interfacial phenomena including SEI formation and the impact of electrolyte additives are receiving special attention in an effort to increase battery longevity and efficiency.

1.2 How Lithium-Ion Batteries Operate

Generally, in Li-ion battery cells, a positive and a negative electrode—both of which are sources of chemical reactions—are separated from one another by an electrolyte solution that contains dissociated salts, allowing ions to move between the two electrodes. Following their external connection, these electrodes undergo simultaneous chemical reactions at both, releasing electrons and allowing the user to tap the current. Lithium ions are transferred in two stages to power lithium-ion batteries. Lithium ions go from the positive to the negative electrode while charging and vice versa when discharging. Li-ion batteries rely on the electrolyte, + ve electrode, and - ve electrodes to work. Carbon makes up the majority of the -ve electrode, metal oxides typically make up the + ve electrode, and lithium salt in an organic solvent serves as the electrolyte[6], [7], [8].

Ion transport through the electrolyte completes the electron flow through the external circuit in order for the battery to function. The electrolyte therefore conducts the ionic component of the chemical reaction between the anode and the cathode (figure 1). A cell's large-area electrodes are separated by a thin separator wetted with electrolyte because the ionic mobility in the electrolyte is significantly less than the electronic conductivity in a metal. A metallic current collector transfers electronic current from the electrodes' redox reactions to and from tabs that are connected to the external circuit. The two electrodes of a rechargeable cell undergo a reversible chemical reaction[9]. Lithium-ion batteries have made it possible for a wide range of energy sectors to utilize them, however interfacial degradation processes and irreversible side reactions continue to limit their performance and lifespan. Among the most important elements influencing these results is the solid electrolyte interphase (SEI) that forms on the anode surface.

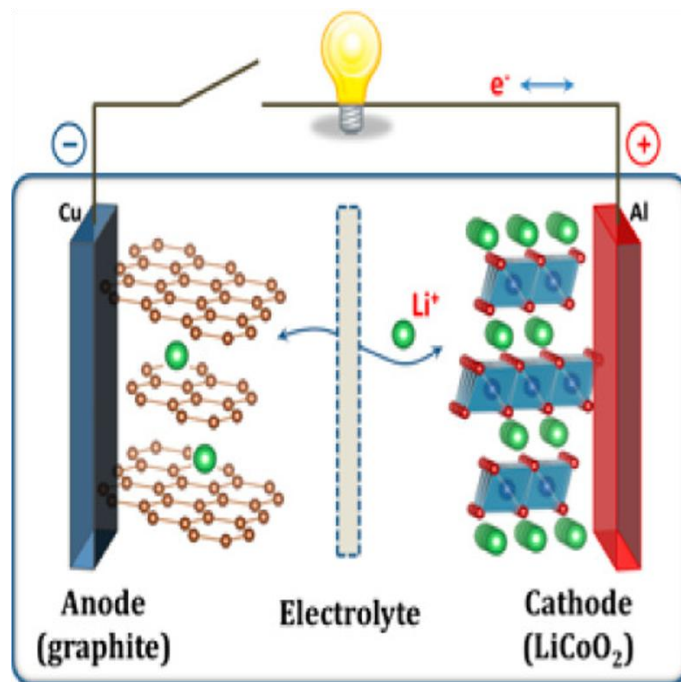


Figure 1 Schematic representation of the original Li-ion battery made of graphite and Li⁺ electrolyte (LiCoO₂) [9]. Reprinted permission from [9]

1.3 Performance Limitations in Lithium-ion batteries and Solid Electrolyte Interface

To create more robust and effective systems, it is crucial to comprehend the limitations of Li-ion batteries, especially those concerning interfacial stability and irreversible capacity loss. We have been utilizing laptop computers to work remotely and cell phones to interact with others. Furthermore, although the user experience has been improved by recent advancements in smartphones and tablet computers, these devices still require thinner, lighter LIBs with higher energy densities to operate for longer periods of time. Furthermore, the demand for lithium-ion batteries that provide better power performance, longer cycle life, and more stored energy is being driven by the drive to decarbonize transportation through the deployment of electric vehicles[9]. Currently, battery electric vehicles (BEVs) powered by Li-ion batteries are the technology of choice to displace traditional internal

combustion engine vehicles (ICEVs). However, charging is still less convenient than refueling [10], [11]. Therefore, widespread EV adoption requires the improvement of fast-charging capability [12]. Batteries gradually lose capacity as they age, which lowers power output, reduces driving range, and degrades user experience. Therefore, increasing reliability and cycle life is essential to preserving EV batteries' long-term dependability and performance[13].

Over time, prolonged cycling and capacity can cause a number of performance issues with lithium-ion batteries (LIBs). Lithium plating, active material loss, electrolyte breakdown, and—most importantly—the development and expansion of the solid electrolyte interphase (SEI) layer on the anode surface are important degradation mechanisms[14], [15].

1.3.1 SEI Formation

A SEI starts to form when an alkali metal is submerged in battery electrolyte, or when a carbon or an inert electrode submerged in the electrolyte is subjected to a negative potential outside of the electrochemical stability window of solid electrolyte. In Li-ion cells, it forms during the initial charge-discharge cycle on the anode. This layer permits Li ions transport across it but obstructs electron flow and inhibits solvent from migrating to the electrode surface. It also controls the kinetics of Li ions which is crucial to fast-charging capabilities. SEI is the primary determinant of the battery's cycle life, safety, power capabilities, lithium deposit morphology, and shelf life. This layer, which is essentially made up of electrolyte breakdown products, is the outcome of the charged anode's reaction with the electrolyte. There are both organic and inorganic products in the SEI. The "medium" for the transport of lithium cations is thought to be the organic SEI. As opposed to the anode material, the inorganic components are thought to be stable against reduction, hence they should be found close to the anode surface. It is believed that the inorganic SEI products are what give the SEI its protective properties. This is somewhat consistent with the original SEI model concept, which suggests that the SEI functions as a

"sieve" that is selectively permeable to the Li^+ cation, the electrochemically active charge carrier; in other words, it behaves like a solid electrolyte for lithium cations but is impermeable to any other electrolyte component that would react with the anode. Inorganic substances such as LiF , LiCl , and Li_2O are frequently the by-products of the reduction of salt anions and precipitate on the electrode surface. The voltage at which the SEI forms in the carbon electrode is dependent upon the type of carbon, the temperature, concentration, and types of solvents, salts, and impurities, as well as the current density and the catalytic properties of its surface (ash content, crystallographic plane type, and basal-to-edge plane ratio). Battery performance is greatly impacted by each SEI parameter and attribute. One undesirable attribute of SEI formation is irreversible capacity loss (ICL), which happens in the first cycle as a result of salt and solvent reduction[14], [16], [17]. Electrolyte additives have been investigated extensively as a viable and efficient strategy to increase SEI stability and lower capacity loss.

1.4 Electrolyte Additives for SEI Modification

It is commonly recognized that the electrolytes of Lithium Batteries are essential to the transfer of lithium-ion (Li^+) during the charging and discharging processes of batteries[18], [19]. Typically, commercial electrolytes consist of three components: solvent (for example ethylene carbonate, EC, and diethyl carbonate, DEC), additives (fluoroethylene carbonate, FEC, and vinylene carbonate, VC), and lithium salt (for example lithium perchlorate, LiClO_4 , lithium hexafluoroarsenate LiAsF_6 , lithium tetrafluoroborate, LiBF_4 , and lithium hexafluorophosphate, LiPF_6). LiPF_6 and other inorganic lithium salts that are commonly used in commercial lithium-ion batteries. Nevertheless, they have a lot of drawbacks. The oxidation process of LiAsF_6 can result in toxic by-products; LiClO_4 's high oxidation property restricts its use; LiBF_4 has poor cycle performance, conductivity, and film-forming properties; and LiPF_6 is thermally unstable, easily reacting with water traces, etc.[20] Many studies have shown

that the use of electrolyte additives can improve rate performance considerably and mitigate lithium batteries from degradation. They improve conductivity, lower charge transfer resistance and encourages the development of a stable SEI[21].

Standard electrolytes are unstable at the electrode's operating voltage during charging, which leads to SEI development at the negative electrode. This ongoing SEI growth prevents Li-ion migration to the active anode material and raises the electrode's overall electrical impedance. Furthermore, some Li^+ may be trapped by the SEI layer, resulting in an initial loss of capacity. Electrolyte additives are the most often used method for addressing this initial capacity loss linked to ongoing electrolyte breakdown[22], [23].

This study investigates potassium hexafluorophosphate (KPF_6) and sodium hexafluorophosphate (NaPF_6) as additives to traditional LiPF_6 -based electrolytes. These salts are less researched than widely used film-forming additives, yet they may affect SEI behavior via changing interfacial processes or lithium-ion transport. The purpose of this study is to examine the effects of these additives on cycling performance, irreversible capacity loss, and SEI generation in both half-cell and full-cell configurations of the graphite-lithium iron phosphate system that is increasing in popularity in BEVs.

1.5 Scope and Objectives of This Work

This thesis' primary goal is to examine the effects of potassium (KPF_6) and sodium (NaPF_6) additives on the electrochemical performance and SEI development of lithium-ion batteries. The goal of the study is to improve long-term cycle stability, increase coulombic efficiency, and decrease initial irreversible capacity loss by adding trace amounts of these salts to the normal LiPF_6 electrolyte.

Using graphite as the anode and lithium iron phosphate (LFP) as the cathode, half-cell and full-cell tests were carried out. To assess battery performance, electrochemical methods including electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), and galvanostatic charge–

discharge cycling were employed. Furthermore, X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) were used to examine surface chemistry and SEI morphology. We hope that this work will help guide future electrolyte design methods for high-performance lithium-ion batteries by shedding light on the ways in which mixed-ion electrolytes affect interfacial stability and overall cell performance.

Chapter 2

Literature review

2.1 Graphite as anode material for lit-ion batteries

A layered, sp^2 carbon, graphite is made up of graphene sheets that are stacked by weak van der Waals forces. In addition to having a high thermal conductivity and excellent in-plane electronic conductivity ($\sim 2.3 \times 10^4$ S/cm), this structure permits reversible Li^+ intercalation between the layers. It provides a high theoretical capacity of 372 mAh/g at a low average voltage (~ 0.1 V against Li/Li^+)[24]. Since 1975, it has been known that molten lithium or compressed lithium powder can be used to create lithium intercalation compounds with graphite up to a maximum lithium content of LiC_6 [25], [26]. In 1983, Yazami and Touzain reported the first successful electrochemical attempt to reversibly intercalate lithium into graphite using a solid polymer electrolyte[27]. Dahn and colleagues discovered in 1990 that the creation of a stable solid electrolyte interphase (SEI) while employing ethylene carbonate (EC) as an electrolyte co-solvent allowed for the reversible electrochemical lithium intercalation to occur even for liquid electrolyte[28]. Not long after, in 1991, Sony brought the first lithium-ion battery to market; nonetheless, it still used coke as an anode and PC as an electrolyte solvent[29]. Since 1994, graphite has served as the active material for the negative electrode in practically all commercial LIBs[30].

The performance of graphite anodes has been progressively enhanced since then, particularly in terms of the first cycle coulombic efficiency, reversible capacity, and cycling stability. One example of this is the discovery of appropriate film-forming electrolyte coatings and additives. Additional advancements in the early 2000s included the creation of sustainable and aqueous electrode processing technologies, which took the place of the hazardous and toxic solvent N-methyl-2-pyrrolidone (NMP)

and binder polyvinylidene fluoride (PVdF), respectively. There will be discussion of recent attempts at research and development[24].

As previously stated, the de-/intercalation procedure basically adheres to the general Daumas and Herold mechanism, with Stage 1 serving as the last stage of the intercalation of lithium ions, meaning that the maximum Li content that can occur under ambient conditions is an overall stoichiometry of LiC_6 [31]. The single graphene layers slip slightly with regard to one another to accommodate the high lithium content. This causes a symmetry change from an ABABA stacking in pristine graphite to an AIAIA stacking in the completely lithiated state (LiC_6 ; where I is the intercalant layer)[32]. Figure 2 depicts the specific de-/lithiation steps. Stages $n = 1\text{L}, 4, 3, 2\text{L}$, and 2 have been seen to occur consecutively for increasing lithium contents before finally reaching Stage 1, for which the extra letter "L" denotes that the lithium ions are arranged more like liquids than perfectly within the layers[33].

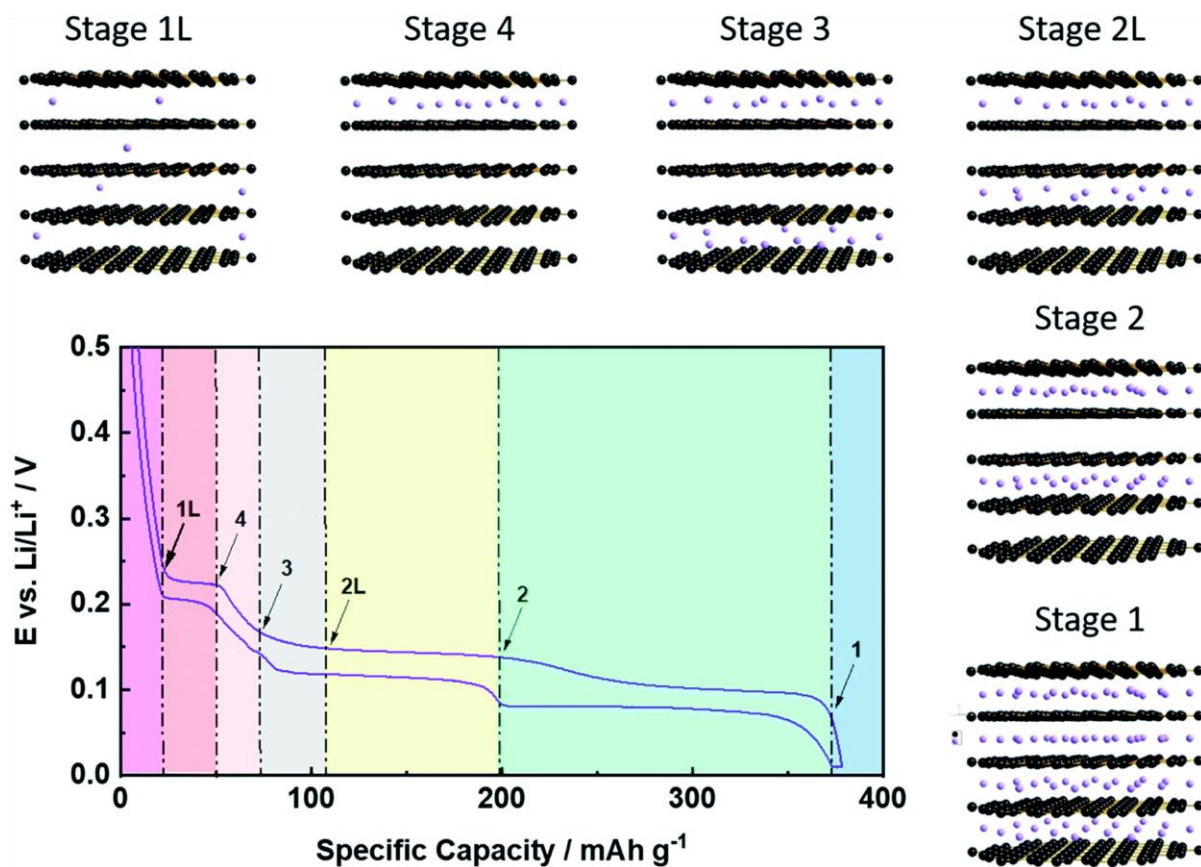


Figure 2 An example of the electrochemical de/intercalation of lithium cations (purple spheres) into graphite via a staging mechanism [24]. Reprinted permission from [24], (open access)

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Stage 1L, the initial stage, is a random, solid-solution-type lithium intercalation that occurs in each interslab of the graphite lattice, or throughout the graphite particle. After that, there is a first-order phase transition from Stage 1L to Stage 4, and then a steep decline in potential leads to the shift to Stage 3. Although this suggests that there is no first-order transition, the precise mechanism is still unclear and may really be fairly complicated[33], [34]. This is also true for the subsequent transition from Stage 3 to Stage 2L, whose appearance depends on temperature and whose precise structure is still up for debate[33], [35], [36], [37]. An increase in lithium content within the same intercalant layers (i.e., every second in the graphite lattice) and improved in-plane ordering are features of the subsequent transition

from Stage 2L to Stage 2[33], [35], [36]. The most well-understood transition is most likely the last (first-order) one to Stage 1, which produces LiC_6 and has the highest capacity fraction[38].

The formation of a stable SEI layer, which inhibits electrolyte breakdown and graphite exfoliation at low voltages, is crucial to graphite's performance as an anode in lithium-ion batteries. Reversible Li^+ intercalation is made possible by EC-based electrolytes, which encourage the production of SEI. In Section 2.3, the key roles of the SEI in capacity and stability will be covered in more detail.

Graphite has a theoretical specific capacity of 372 mA h/g, which is below the capacity of the most promising conversion- or alloying-type anodes but higher than the capacity of the majority of cathode materials[39]. Nevertheless, the final energy density at the full-cell level—which is dependent on both cell voltage and capacity—is an element that is commonly disregarded. In this sense, graphite has a distinct advantage over these substitutes since, aside from metallic lithium, it has the lowest average de-/lithiation potential (i.e., 0.2 V vs. Li/Li^+)[24]. A recent study by Andre et al[40] examined the effects of several anode materials on the practical full-cell energy densities in full-cells. This study shows that graphite is still utilized in the majority of commercial lithium-ion batteries since most other anode materials would have lower energy densities than graphite. Energy efficiency, or the ratio of stored energy to released energy upon discharge, is another factor that is often overlooked. It is directly related to the difference between the charge and discharge potential (assuming a constant coulombic efficiency). While some progress has been reported recently for (pre-lithiated) conversion/alloying-type materials when limiting the de-/lithiation to a rather narrow potential range, graphite's relatively small voltage hysteresis makes it an even more favorable alternative to most alternatives studied thus far[41].

First cycle irreversible capacity (C_{irr}) is a significant problem for graphite anodes in LIBs because of the reductive electrolyte breakdown and consequent Li^+ use as the charge carrier. Altering the surface

of the graphite particles is one method of lowering the C_{irr} that has been used since graphite-based LIBs were commercialized. Such surface modification can use gases, ceramic materials, or (oxidative) solutions to treat the graphite particles, usually followed by a heat treatment. In order to improve the electrochemical performance, both the edge and basal planes undergo chemical changes. Another strategy is based on adding electrolyte additives that kinetically promote the production of SEI more effectively, hence enabling the initial coulombic efficiency (ICE) to be increased[24]. Second approach will be discussed in section 2.4.

Because graphite has a low de-/lithiation potential near the plating of metallic lithium, it is particularly vulnerable to ageing from both storage (calendar ageing) and use (cycling). This problem fundamentally affects all battery materials[42], [43]. In their thorough summary of the possible aging mechanisms for graphite, Vetter et al. offered a general classification, distinguishing between ageing processes based on (i) the (long-term) instability of the SEI, (ii) lithium plating, and (iii) the contribution of electrochemically inactive electrode components like the current collector, conductive additives, and binder. Regarding possible safety concerns as well, they thought the first two were the most important of them[42]. The initial cycles are the primary, though not the only, times when the SEI is formed. The composition and morphology of the SEI continue to evolve during cycling and storage. This temperature-related change in the SEI causes the electrolyte to be consumed, lithium to be continuously lost, and resistance to rise as a result.

Three crucial phases of harmful interactions between graphite anodes and electrolytes were found by Feng et al[44]. Initially, heat from overcharging or high current densities causes SEI breakdown to start at temperatures as low as 57 to 90 °C. In the second stage (120–250 °C), SEI renewal and decomposition take place at the same time, creating a thicker but marginally stabilizing layer. Graphite collapse and electrolyte degradation cause the SEI to entirely degrade over 250 °C, resulting in thermal runaway and

significant safety hazards. Graphite surface modifications and SEI-forming additives have been the subject of extensive investigation in an effort to stop this.

Natural graphite (NG) and synthetic graphite (SG) are the two main types of graphite utilized in cutting-edge LIBs. The particles are polycrystalline in both of them and made up of many single-crystalline domains; the size of these domains determines whether the graphite is micro- or macro-crystalline[45]. However, as Figure 3 clearly shows, these domains are more randomly oriented in SG than they are in NG, where they are frequently orientated in the same direction.

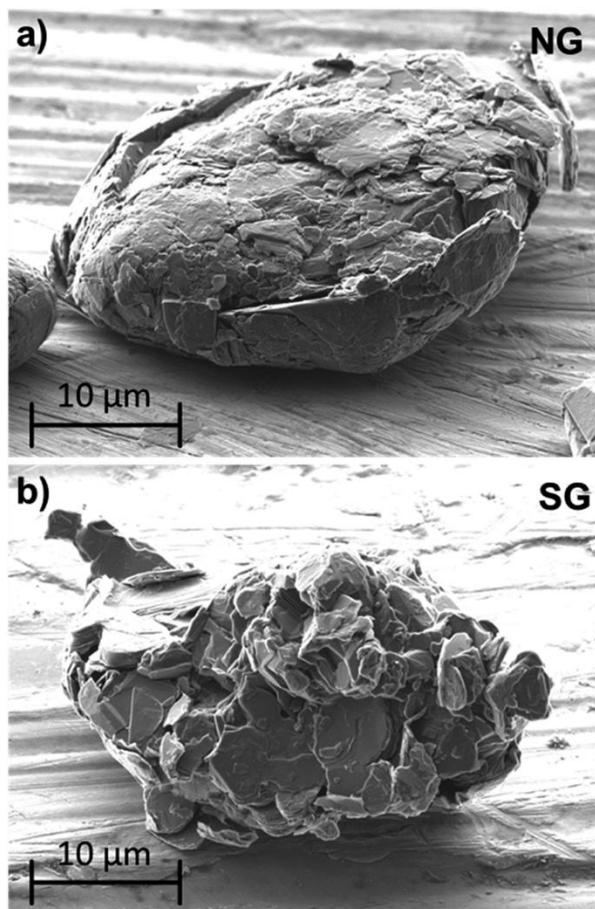


Figure 3 SEM images of synthetic graphite (SG) and sphere-shaped natural graphite (NG) are compared [24]. Reprinted permission from [24], (open access)

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In reality, the initially flake-like NG particles and the often irregularly shaped SG particles must undergo spheroidization, an additional mechanical treatment, following the mining process, in order to get such a spherical particle shape (also known as "potato shape")[46]. In order to decrease the surface area and enhance the ICE by lowering the reductive electrolyte breakdown and further inhibiting solvent co-intercalation, a thin carbon coating is commonly applied after this mechanical process[47].

Although the final performance of any given graphite material ultimately depends on a number of variables, the two types share a number of general traits: In essence, SG is made by heating unsaturated carbon—which is often obtained from petroleum—to 2500 °C for a set amount of time, sometimes even days[48]. Compared to NG, which is characterized by larger, more anisotropically oriented crystalline domains, smaller domain sizes and a correspondingly higher fraction of domain interfaces result in lower capacities[49]. Currently, both materials are utilized for commercial LIBs[50], [51].

Graphite's favorable electrochemical characteristics, structural stability, and compatibility with commercial electrolytes continue to make it the most used anode material in lithium-ion batteries. Nonetheless, the solid electrolyte interphase (SEI), which protects the graphite surface and permits reversible lithium intercalation, is crucial to its stability and performance. The role of electrolyte additives and SEI behavior will be further examined in the upcoming sections to illustrate the continuous efforts to improve the performance and interfacial stability of graphite-based anodes.

2.2 Lithium iron phosphate (LFP) as cathode material for lithium-ion batteries

Due to its direct influence on electrochemical performance, the cathode is considered a crucial part of lithium-ion batteries (LIBs) and a factor of commercialization[52], [53]. Sony introduced layered oxide LiCoO_2 as the first-generation cathode material in 1991 together with the C_6Li anode. Later, various

types of materials have appeared in recent decades, including spinel oxides (LiMn_2O_4), polyanion oxides (LiFePO_4), Li-rich layered oxides, layered transition metal oxides ($\text{LiNi}_{1-y-z}\text{Mn}_y\text{Co}_z\text{O}_2$), etc.[54], [55], [56]. Although high-energy-density battery materials are being sought after, safety remains the top priority for battery systems used in electric vehicles (EVs) and portable electronics. Because of its exceptional safety characteristics, LiFePO_4 has been the subject of both scientific and industrial investigation since Goodenough et al.'s initial paper in 1997[57]. Additionally, LiFePO_4 is a favorable cathode material for commercial LIBs due to its moderate operating voltage (3.5 V vs. Li/Li^+), moderate capacity (170 mAh/g), flat voltage plateau, available material supply, low material cost, and good environmental compatibility. Low ionic diffusivity (ca. 10^{-11} – 10^{-10} S cm^{-1}), poor low temperature performance, low volumetric energy density, and poor electronic conductivity ($>10^{-9}$ S cm^{-1}) are thought to be the primary barriers to its broader use[58].

LiFePO_4 has an orthorhombic lattice structure and is a member of the olivine family of cathode materials in the space group Pnma. Phosphorus atoms and iron/lithium occupy tetrahedral and octahedral sites, while oxygen atoms are arranged in a hexagonal-close-packed configuration. This results in corner-shared FeO_6 octahedra and edge-shared LiO_6 octahedra parallel to the b-axis. With the PO_4 tetrahedra connecting the two octahedra, 3D spatial network structures known as α - LiFePO_4 are formed[59]. Delithiation results in the appearance of the FePO_4 phase in the single crystal structure, which is nearly identical to LiFePO_4 in terms of crystalline structure (Fig. 4). The volume change content is only 6.81% up to the fully charged state, preventing capacity deterioration caused on by volume fluctuations over extended cycles[57]. Because of its strong P–O covalent connection and low volume variation, LiFePO_4 exhibits good safety, cyclability, and thermal stability[60].

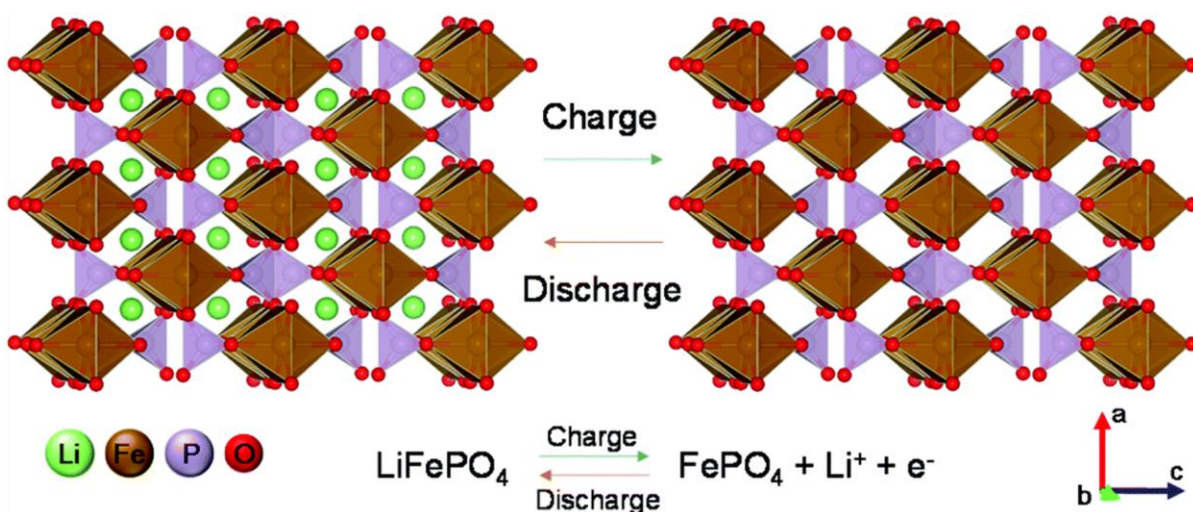


Figure 4 Schematic of LiFePO₄ and FePO₄. Delithiation converts LiFePO₄ to FePO₄ during charging. Through lithiation FePO₄ undergoes a reversible conversion to LiFePO₄ during the discharge process [60]. Reprinted permission from [60]

According to the Gibbs phase rule, the two-phase $\text{LiFePO}_4 = \text{FePO}_4 + \text{Li}^+ + \text{e}^-$ reaction that arises from the slight deformation of the LiFePO_4 host framework upon the removal of Li produces a flat $V = 3.45$ V *versus* x in Li_xFePO_4 . This voltage falls inside the carbonate electrolyte window, providing the LiFePO_4 cathode with exceptional electrochemical stability and no noticeable capacity loss after 1000 cycles.

According to several research, layered metal-oxide cathodes (such LCO, NMC, and NCA) are not as safe as LFP cathodes. For example, Zaghib et al.'s differential scanning calorimetry (DSC) investigations revealed that Li metal oxides start exothermic breakdown beyond about 200 °C, but LFP does not experience a rapid exotherm until very high temperatures. Similarly, Bugryniec et al. found that LFP cells are considerably more thermally stable than NMC cells under mistreatment after comparing them in oven experiments[61], [62], [63]. The main factors that make LFP preferred for large-scale applications are its excellent stability and non-toxicity[64], [65]. Due to its affordability

and safety, LFP is now used by many significant EV manufacturers for standard-range vehicles. Interestingly, in 2021, Chinese manufacturing of LFP EV batteries overtook that of NMC batteries[66]. Since its discovery in 1997, numerous researchers have attempted to enhance this material's performance using a variety of techniques. Two approaches will be briefly discussed.

To increase the electronic conductivity, LiFePO_4 particles are frequently coated with conductive Li^+ and electron materials. Since carbon is always deposited in situ on the surface of LiFePO_4 particles during synthesis in a reducing environment, carbon coating is the most effective method. Armand et al.[67], [68] conducted the groundbreaking research, demonstrating that LiFePO_4 coated with carbon can get nearly the theoretical capacity. Chiang et al. (2002)[69] reported that they used low-level doping with various supervalent cations (Nb^{5+} , Ti^{4+} , W^{6+}) to increase the electronic conductivity of bulk LiFePO_4 by 8 orders of magnitude to $10^{-2} \text{ S cm}^{-1}$, which is similar to that of LiCoO_2 and LiMn_2O_4 . The resultant nanoparticles exhibited a capacity that was nearly identical to the theoretical one at low charge/discharge rates. At rates as high as 10 C, the capacity maintained above 80 mAh/g with minimal polarization.

For lithium-ion batteries, lithium iron phosphate (LFP) is a particularly stable, secure, and affordable cathode material. It is the perfect material for applications like grid storage and electric vehicles where durability and safety are top priorities because of its olivine structure, extended cycle life, and thermal robustness. Even though LFP has a lower energy density and intrinsic conductivity than layered oxide cathodes, its rate performance and electrochemical efficiency have been greatly improved by ongoing developments such as metal ion doping, carbon coating, and nano structuring. These continuous advancements guarantee that LFP will continue to be a popular and competitive cathode material in modern battery technology.

2.3 The solid electrolyte interface (SEI)

A solid electrolyte interphase (SEI) layer, also known as a "solid electrolyte interface," develops on the surface of graphite, the most widely used anode material, during LIB operation as a result of side reactions with the electrolyte solvent and salt. It is well acknowledged that the SEI layer plays a crucial role in LIB performance, influencing its self-discharge properties, cycle life, rate capability, safety, and initial capacity loss. Although the anode SEI layer is essential, its growth and production are difficult to regulate because of the many variables that affect its stability, shape, and chemical composition. Graphite type, shape, electrolyte composition, electrochemical conditions, and cell temperature are some of these variables. Therefore, the development of LIB technology should focus primarily on the generation of SEI layers and electrochemical stability during extended periods of operation[70].

The total amount of lithium available for creating the SEI and initial charging of the cell is known as the "lithium inventory" of the cathode and electrolyte salt, and it forms the anode SEI layer. The energy and power density of a LIB and the optimal surface area of the anode must be carefully balanced. To stop additional undesirable breakdown of the electrolyte, which consumes Li ions, the SEI layer must cover the entire anode surface. While losing Li ions from the electrolyte reduces liquid-phase mass transfer and raises electrolyte resistance, which lowers power density, the quantity of Li ion loss from the cathode directly impacts the first-cycle irreversible capacity (energy density)[71], [72]. Ten percent of the initial capacity is often used up in irreversible SEI development during the first full cycle[73]. Gaining a better knowledge of the composition and shape of the most advanced graphite SEI layers is crucial to developing enhanced SEI layers that stop electrolyte from continuously decomposing on graphite surfaces. Because of their instability at the anode potential operating window, the precipitates from reduced breakdown of solvents, salts, lithium ions, and contaminants in the electrolyte make up the anode SEI layer[71], [74]. It mostly occurs at the initial charge, but after the first cycle, it continues

to form gradually until the SEI layer is fully established, which makes contemporary LIB construction processes more complex. An ideal SEI layer should have high permeability and selectivity for lithium ions, little electrical conductivity, and strong resistance to electrolyte diffusion. Since electrons cannot move to or through the layer once it is properly formed, additional decomposition reactions with salts and solvents are inhibited (the increased electronic resistance moves the surface potential to within the electrolyte stability window and increases the potential on the graphite surface). Since electron exposure to the electrolyte or electrolyte diffusion to the graphite surface causes the SEI layer to gradually thicken during repeated charge-discharge cycles, the growth in layer thickness after a few charge-discharge cycles is not nearly as large as it was during the first cycle. The layer gradually thickens, increasing cell resistance and further consuming Li ions, solvents, and salts. Throughout the formation cycling process, the SEI layer keeps growing, which reduces cell capacity and Coulombic efficiency[70].

The production of SEIs typically takes days due to slow scan rates, which range from $\sim \pm C/5$ to $\sim \pm C/20$, which create a denser structure instead of a very porous one. Formation cycles are typically repeated at various scan rates and/or temperatures to create high-quality SEI layers following the initial charge-discharge cycle. The process becomes more costly as the duration and number of charge-discharge cycles grow, which also either reduces the pace of cell production or raises capital costs (i.e., more cycling stations are needed). Lowering the SEI formation time would result in increased production rates without requiring additional energy, space, or equipment, thereby lowering the cost of battery packs and plants[75], [76].

The most popular electrolytes in LIBs are an aprotic salt solution and low-molecular-weight organic solvents. The graphite anode causes these electrolytes to decompose, and the resulting SEI layer determines the cell's initial performance as well as its capacity fade characteristics over time. Thus, the

question is whether electrolyte breakdown can be reduced or managed to ensure consistent cell functioning. The relative electron energies of a thermodynamically stable redox pair in a LIB's anode, electrolyte, and cathode are displayed in Fig. 5. μ_A and μ_C represent the anode's and cathode's electrochemical potentials, respectively. The difference between the electrolyte's LUMO (lowest unoccupied molecular orbital) and HOMO (highest occupied molecular orbital) energy is known as the stability window. The window is displayed as Eg. Reduced electrolyte results from μ_A being above the LUMO energy, while oxidized electrolyte results from μ_C being below the HOMO energy. To raise the energy density of the redox pair, the anode and cathode must have the greatest possible energy separation. The oxidation and reduction potentials of the organic electrolytes employed in LIBs are approximately 4.7 V vs. Li^+/Li and 1.0 V vs. Li^+/Li , respectively. Li's intercalation potential into graphite is below the electrolyte's reduction potential, ranging from 0 V to 0.25 V vs. Li^+/Li . As a result, while charging, the potential of the graphite electrodes drops below the electrolyte's stability window and breaks down at the graphite surface to generate the SEI[74].

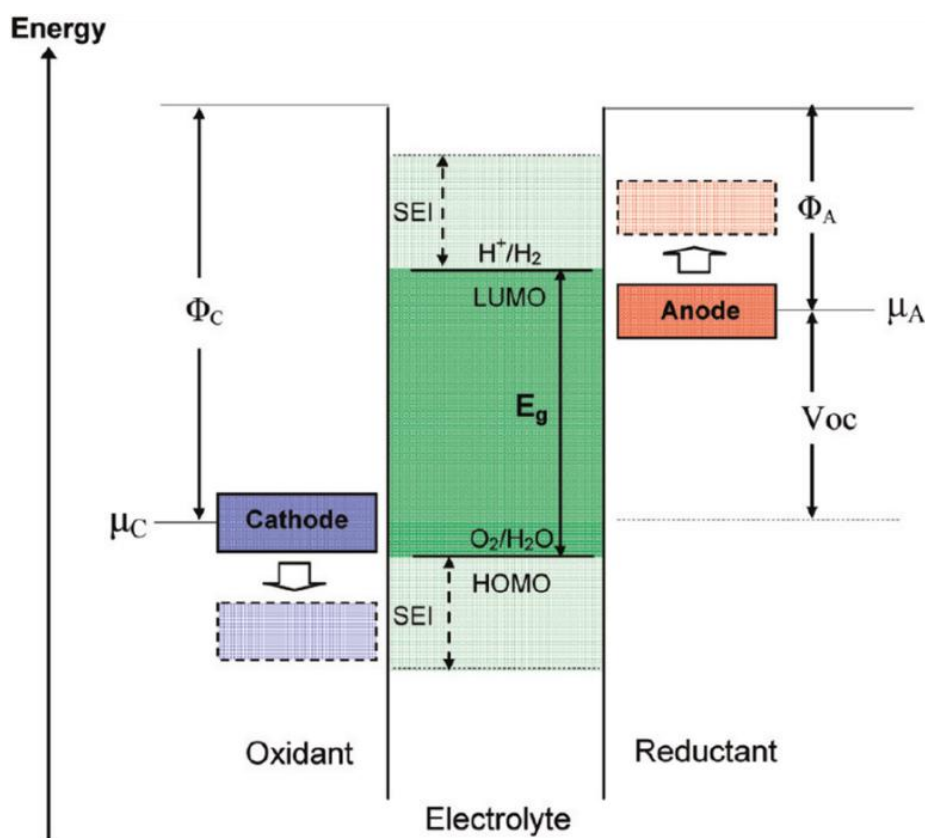


Figure 5 Energetics of the anode and cathode SEI layer development under electro-oxidation and electro-reduction circumstances [74]. Reprinted permission from [74]

In order to minimize irreversible capacity loss and limit the loss of lithium inventory to the first few cycles, the chemical composition of the SEI should contain stable and insoluble compact inorganic compounds like Li_2CO_3 instead of metastable organic compounds like $ROLi$ and $ROCO_2Li$ (where R is a low-molecular-weight alkyl group). High-capacity retention depends on the decomposed SEI components' insolubility in an electrolyte because losing them could cause new SEI to develop where they dissolved out[77], [78]. Historically, the SEI has been considered to have a structure of the bilayer kind. It is believed that the layer close to the electrolyte contact is less dense and porous, filled with electrolyte and containing a significant amount of organic material. In a subsequent cycle, the shape of this outer, organic layer may vary due to more reduction. It is assumed that the inorganic compounds

that shield the anode surface and stop reduction make up the majority of the inner layer next to the graphite. It is therefore thought to have a denser morphology and less porosity. Although the SEI structure appears to be a bilayer structure in recent investigations, it is actually more complex[79], [80], [81], [82].

Lu et al[83], [84]. investigated how the SEI's morphology changed throughout its creation. SEM micrographs at two distinct magnifications of the graphite anode surface from their investigation at varying polarization levels during the initial charge are displayed in Fig. 6. As the anode's potential shifted in the direction of the intercalation potential, the SEI thickness grew during the formation cycle. Their model indicated that loosely held organic polymer components made up the majority of the SEI at the start of the production process. The SEI layer changed into a denser inorganic salt structure when the voltage was reduced. Figures 6 and 7 depict this morphological change[83], [85].

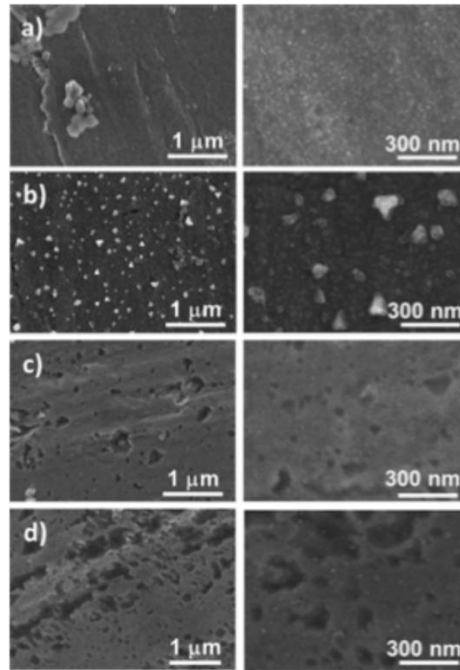


Figure 6 SEI morphology at different formation potentials (a) 0.7 V, (b) 0.5 V, (c) 0.3 V, and (d) 0.0025 V, as described by Lu et al. The photos in the right column are magnified to a greater extent (100,000x) than those in the left column (30,000x) [84]. Reprinted permission from [84]

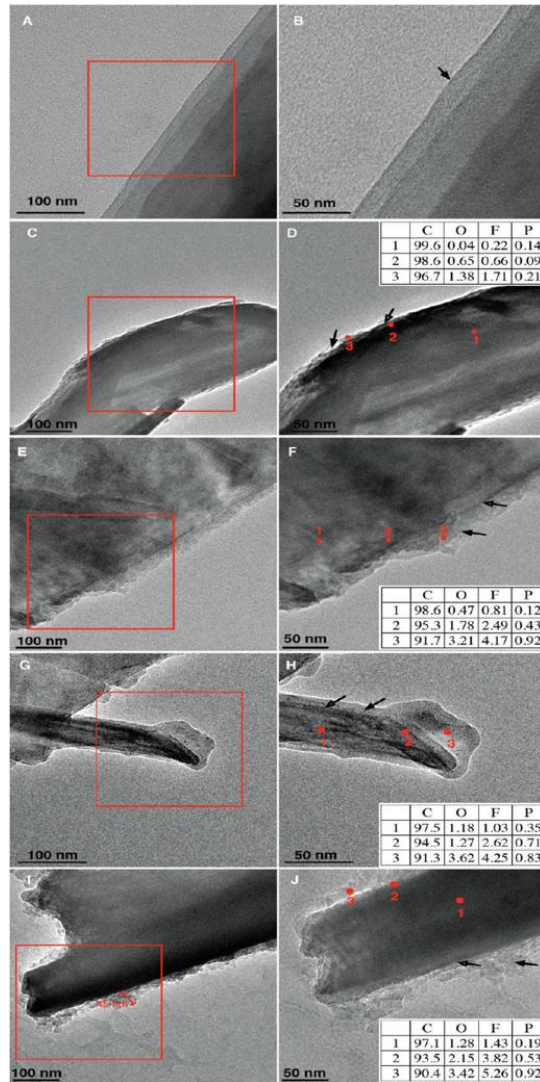


Figure 7 TEM images of fresh graphite and SEI on graphite anodes cycled to four cutoff voltages in 1.2M LiPF₆/EC during first charge reported by Lie et al., (A and B) Fresh graphite electrode, (C) 1.3, (E) 0.6, (G), 0.1, and (I) 0.05 V [85]. Reprinted permission from [85]

SEI generation is strongly influenced by temperature, electrolyte salt content, and reduction current rate[86]. It is challenging to analyze the mechanism of SEI production when all of these variable variables are combined. It is widely acknowledged, therefore, that following reduction, LiPF₆ precipitates as LiF or Li_xPF_y. Li₂CO₃, lithium alkyl carbonate (ROCO₂Li), or other organic compounds are formed when carbonates from the electrolyte solution precipitate with lithium ions. LiF, Li₂O,

Li_2CO_3 , and other insoluble products may diffuse back into the electrolyte, whereas other soluble chemicals from solvent breakdown may stay on the graphite surfaces as parts of SEI layers. The majority of reduction activities on highly ordered graphite occur between 0.8 V and 0.2 V vs Li/Li^+ . When the SEI is not fully established, the solvent and lithium ions co-intercalate into the graphene planes, causing reduction to continue below 0.2 V. Continuous exfoliation may prevent the SEI layer from developing completely if this co-intercalation is too great. These procedures are shown visually in Fig. 8 [70].

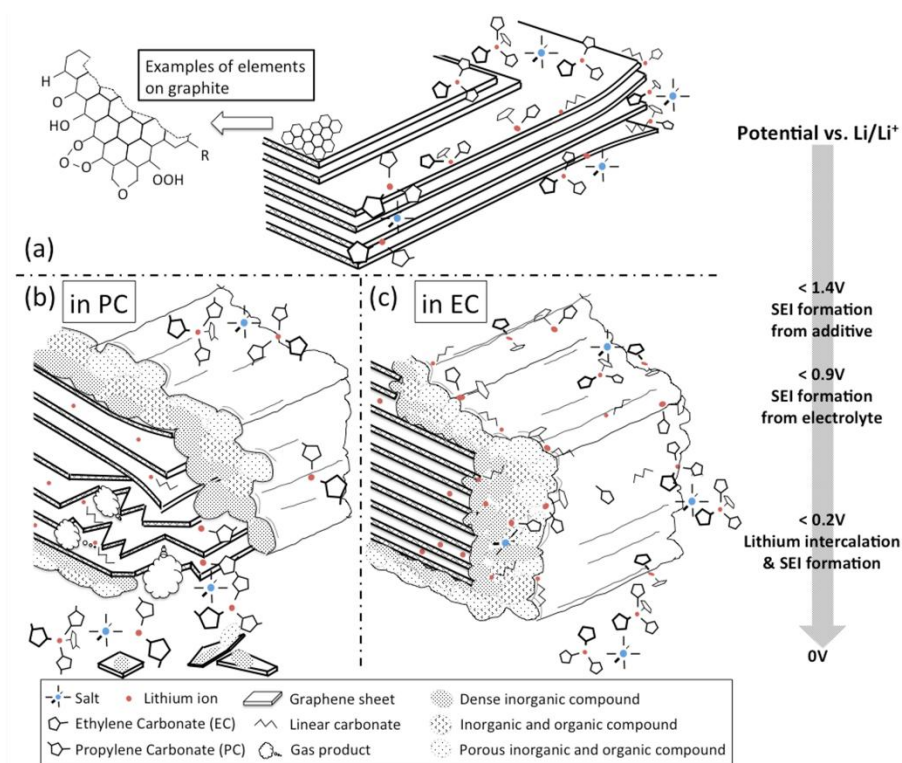


Figure 8 Anode SEI formation process diagram illustrating (a) graphene layers encircled by electrolytes salts and solvents above 1.4 V vs. Li/Li⁺, (b) propylene-carbonate (PC) intercalating with lithium ions into graphene layers to produce exfoliations below 0.9 [70]. Reprinted permission from [70], (open access), <https://creativecommons.org/licenses/by/4.0/>

The SEI has been analyzed using a range of instruments and methodologies, including conventional electrochemical techniques like cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The surface characteristics and morphology of the SEI have been imaged using the conventional techniques of atomic force microscopy (AFM)[87], scanning electron microscopy (SEM)[88], [89], transmission electron microscopy (TEM)[90], [91], scanning tunnelling microscopy (STM)[92], [93], and ellipsometry[94]. Since the anode SEI is a thin layer over graphite, surface analysis techniques including Fourier transform infrared spectroscopy (FTIR)[95], [96] and X-ray photoelectron spectroscopy (XPS)[97], [98], [99] have been used for characterization due to their chemical identification capabilities and surface sensitivity.

To summarize, the solid electrolyte interphase (SEI) is essential for maintaining the stability of lithium-ion batteries because it shields the anode surface, facilitates lithium-ion transport, and reduces electrolyte decomposition. Its composition, structure, and characteristics have a direct impact on battery performance, including cycle life, rate capability, and capacity retention. Therefore, it is crucial to comprehend and modify the SEI, particularly through electrolyte composition and additives, in order to advance battery technology. This thesis's experimental work is based on this understanding.

2.4 Electrolyte additives for li-ion batteries

Li-ion battery performance is significantly impacted by the composition of the electrolyte in terms of general electrochemical characteristics, electrode stability, cycle life, long-term stability and safety. In order for modern batteries to have effective electrolyte systems, additives are necessary components. One of the most practical and affordable ways to enhance Li-ion batteries is through the use of electrolyte additives. Additives typically make up no more than 5% of the electrolyte's weight or volume. Additives can: (1) help solid electrolyte interface/interphase (SEI) form on graphite surface; (2) decrease irreversible capacity and gas generation for SEI formation and long-term cycling; (3) improve LiPF_6 's thermal stability against organic electrolyte solvents; (4) prevent cathode material from dissolving and overcharging; and (5) improve electrolyte physical properties like ionic conductivity, viscosity, wettability, and so on[100], [101].

One or more lithium salts, such as perchlorate (LiClO_4), tetrafluoroborate (LiBF_4), or hexa fluorophosphate (LiPF_6), combined with organic carbonate-based non-aqueous solvents like propylene carbonate (PC), ethylene carbonate (EC), diethyl carbonate (DEC), or ethylmethyl carbonate (EMC), make up the electrolytes. LiPF_6 is one of the most extensively utilized lithium salts because of its strong ionic conductivity and electrochemical performance[102], [103], [104].

When choosing additives for LIB electrolytes, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) values have a significant impact. These orbitals are crucial for figuring out the stability, reaction potential, and performance of the additive at the interface between the electrode and electrolyte. **HOMO Level and Oxidative Stability:** The additive's oxidation potential is determined by its HOMO level. Low HOMO additives are less likely to oxidize at the cathode's high voltage ranges, which is essential for preserving the stability of the electrolyte. By oxidizing at the right voltage, additives can create a stable cathode electrolyte interphase (CEI) that shields the cathode from deterioration and prolongs the battery's cycle life. **LUMO Level and SEI Formation:** The additive's reduction potential is controlled by the LUMO level. By taking part in reduction processes close to the anode, additives with high LUMO levels can create an SEI that shields the anode from adverse reactions. A well-constructed SEI layer stabilizes the anode during cycling and minimizes the electrolyte's ongoing breakdown. The electrolyte's electrochemical window can be expanded by adding additives chosen for their HOMO and LUMO values. This enables the electrolyte to function steadily at greater voltages without experiencing unintended side effects. **Prevention of Unwanted Side Reactions:** Additives with the right HOMO and LUMO levels can be carefully selected to avoid unwanted electron transfer reactions, which could otherwise shorten battery life and deteriorate the electrolyte. For instance, the SEI generation can be stabilized by an additive with a well-matched LUMO without encouraging more reductions that might harm the anode[105], [106], [107], [108].

2.4.1 Film-forming additives

Depending on their particular purposes, several additives are used: Fluoroethylene carbonate (FEC) and vinylene carbonate (VC) are examples of film-forming additives that help produce and stabilize the SEI on the anode and the CEI on the cathode, lowering side reactions and extending cycle life[109].

2.4.2 Conductivity and functional additives

Conductivity enhancers, such as lithium bis(oxalato)borate (LiBOB), increase the electrolyte's ionic conductivity, which raises the battery's power capacity[110]. Triphenyl phosphate (TPP) and tris(2,2,2-trifluoroethyl) phosphate (TFEP) are examples of flame retardant chemicals that are used to increase the safety of LIBs by lowering the possibility of thermal runaway[111]. By raising the internal resistance when the voltage beyond a predetermined threshold, overcharge prevention additives such as biphenyl (BP) and cyclohexylbenzene (CHB) stop overcharging[112]. Low-temperature performance enhancers, such succinonitrile (SN) and lithium difluoro(oxalato)borate (LiDFOB), increase cycling stability and performance at low temperatures[113]. Other types of additives would be SEI modifier which was the focus of this study and will be discussed further in details.

The use of additives has drawbacks as well. During battery operation, certain additives may break down, producing gases or other byproducts that over time may impair battery performance. Furthermore, the price of additives may raise the battery's total cost, and determining the best chemical concentration and mix may be difficult and necessitate a lot of study and experimentation. Despite certain obstacles, additives' benefits for enhancing LIB performance and safety frequently outweigh their drawbacks, making them a crucial component of developing battery technology[114].

2.4.3 Boron-based additives

Compounds containing boron have become attractive options for electrolyte additions because of their special chemical structure and versatility. Chemicals called boron additives, which are utilized as electrolyte additives in lithium-ion batteries, include boron atoms. Because they improve thermal stability, avoid side reactions that could degrade electrodes and electrolytes, and generate stable interphases on the electrode surfaces, these additives are essential for boosting battery performance. Strong SEI layers on the anode and CEI layers on the cathode can be formed more easily with boron

additions. To extend the life cycle and preserve battery efficiency, these interphase layers are crucial for shielding the electrodes from additional electrolyte breakdown[115], [116]. These additives can promote the breakdown of lithium salts like LiPF_6 by interacting with PF_6^- and F^- ions in electron-deficient environments. For instance, Zou et al.[117]found that adding Tris(trimethylsilyl)borate (TMSB) as an electrolyte addition greatly enhanced the capacity retention and cycling performance of Li/NCA cells. Notably, after 200 cycles at 1C, the cell containing 1% TMSB maintained 86.0% of its capacity, but the baseline electrolyte only maintained 67.2%, indicating that TMSB is effective at reducing impedance and mitigating deterioration (Figure 9).

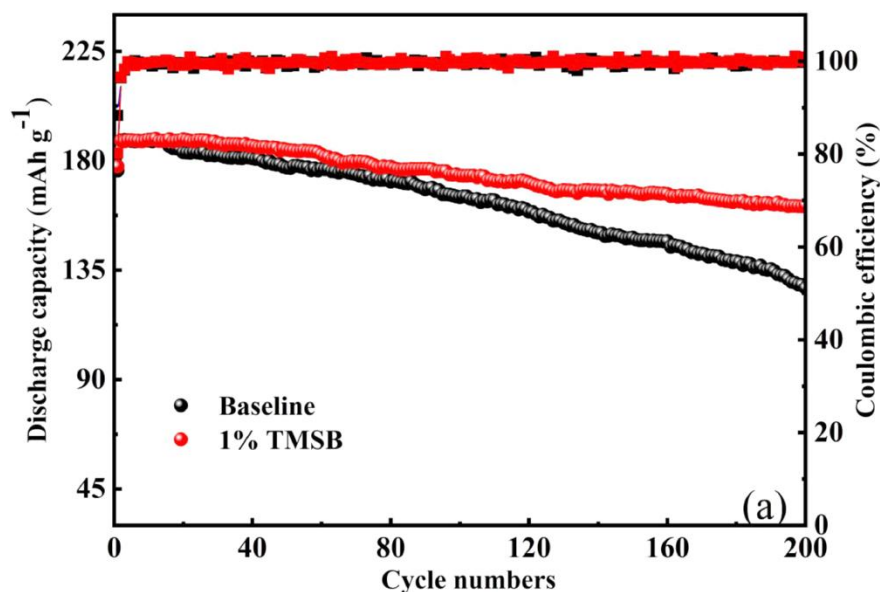


Figure 9 Cycling performance of Li/NCA cells with and without TMSB additive[117].

Reprinted permission from [117]

2.4.4 Sulfur-based additives

In another study by Li et al.[118]they employed ethylene sulphate (DTD), a sulfur-based addition, as a new electrolyte additive for graphite anode material that forms films. Their SEM photos demonstrated that when DTD is added to the electrolyte, the graphite surface develops a smoother and more uniform

surface coating. As a result, the Li/graphite half cells that were cycled in an EC-based electrolyte with DTD showed better cycling capability and a greater specific capacity than those that were not.

2.4.5 Alkali metal salt additives (Na^+ and K^+ salts)

There are also some electrolyte additives that modify the SEI. For instance, there have been attempts to enhance SEI formation using alkali metal salts. According to Komaba et al.[119], adding 0.22 M NaClO_4 to a 1 M LiClO_4 1:1 (vol.) EC–diethyl carbonate (DEC) electrolyte clearly decreased the initial irreversible capacity and improved capacity retention. Comparing the SEI produced with and without sodium ions, the former is more homogeneous and exhibits significantly lower resistance. Alternatively, it has been explored for improving SEI production by pretreating graphite materials with sodium salts that are insoluble in organic electrolytes, such as LiCl and Na_2CO_3 [120]. Such a pretreatment resulted in a little increase in the potentials of intercalation and de-intercalation of Li^+ ions with graphite, as shown in Fig. 10, in addition to improving capacity retention and reversible capacity.

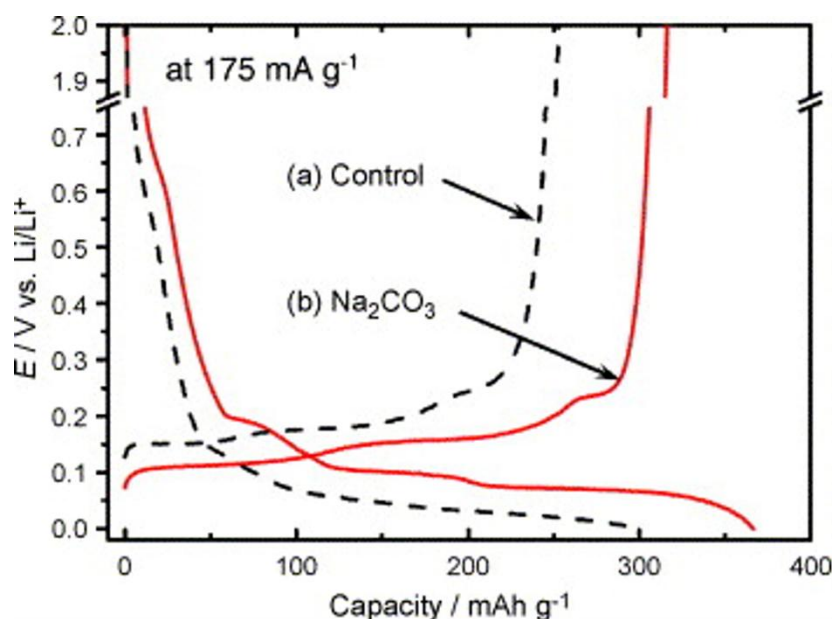


Figure 10 First cycle voltage profiles of the graphite electrodes in a 1M LiClO₄ 1:1 EC-DEC electrolyte with (a) and without (b) pretreatment using a 5.0% wt Na₂CO₃ aqueous solution [120]. Reprinted permission from [120]

Zheng et al.[121]The 1 M LiClO₄ EC–DEC system demonstrated a clear enhancement by K⁺ ions, demonstrating that the addition of a little amount of K₂CO₃ greatly enhanced the reversible capacity of graphite and enhanced the rate capability of the cell. According to Zheng et al.'s Raman spectroscopic research, the addition of a K salt reduced the solvation of Li⁺ ions by EC molecules, reducing solvent breakdown and forming a thinner and more porous SEI. Significantly reduced surface resistance and charge-transfer resistance have validated the latter.

Moharana and colleagues [122]the ideal concentration of KPF₆ to enable a thin LiF-rich SEI film and speed up Li⁺ transit is 0.001 M. Potential electron leakage paths for Li⁺ reduction to Li metal is blocked by higher LiF concentration. Furthermore, the defect sites for favorable Li dendritic nucleation are blocked by the reduced desolvation energy and quicker diffusion rate of K⁺ in the electrolyte. A dendritic-free, faster-charging graphite anode is produced by both of these techniques working together,

and this can have a significant impact on the creation of better high-rate cell chemistries. Li et al.[123]investigated the potential of NaClO_4 as a high-energy Li-ion battery electrolyte additive. They found out that with just 0.1 %wt of NaClO_4 added, Li-rich/graphite full cells can sustain 86% of their capacity after 50 cycles, while Li-rich/Li half cells can sustain 95% of their capacity after 100 cycles, demonstrating a wide range of possible applications. Figure 11 (a) and (b) demonstrates the cycling performance of these half and full cells respectively.

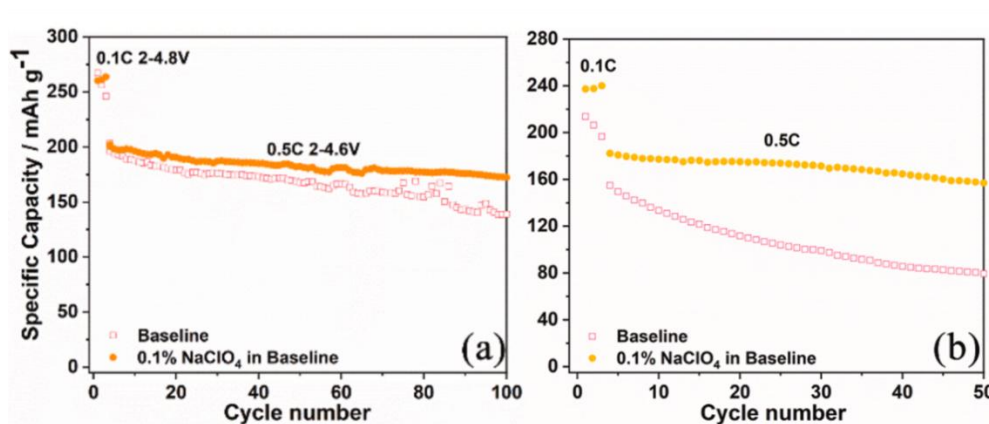


Figure 11 Cycling performance of half cells batteries (a) and full cells (b) with and without 0.1% NaClO_4 additive. Cells were cycled at 0.5C [123]. Reprinted permission from [123]

The performance, safety, and longevity of lithium-ion batteries can all be enhanced with the use of electrolyte additives. These additions can improve cycle stability, increase coulombic efficiency, and drastically minimize irreversible capacity loss by altering the composition and development of the solid electrolyte interphase (SEI). The concentration of an additive and how it interacts with the electrolyte and electrode materials determine its efficacy in addition to its chemical composition. The subject of electrolyte additives is broad and always changing, even though this section covered a few sample compounds and their modes of action. Many additional substances are being researched in various battery chemistries and application scenarios, each with distinct roles and impacts. Although a thorough analysis of all currently existing or developing additives is outside the purview of this report, the studies

that are mentioned here show how important electrolyte engineering is to the advancement of lithium-ion battery technology.

2.5 Research Gap

While there has been some investigation[119] into the use of inorganic additives like potassium hexafluorophosphate (KPF_6) and sodium hexafluorophosphate (NaPF_6) in lithium-ion battery electrolytes, previous studies have mainly consisted of initial observations in half-cell configurations and lacked thorough electrochemical and physicochemical analysis. Few studies, specifically, have used sophisticated characterization techniques like electrochemical impedance spectroscopy (EIS) and X-ray photoelectron spectroscopy (XPS) to assess the effects of these additives on solid electrolyte interphase (SEI) composition, cycle life, or impedance evolution. These gaps show that in order to fully comprehend the relationship between inorganic additive chemistry and SEI stability, a more methodical investigation is required. More significantly, the use of KPF_6 and NaPF_6 additives in full-cell systems represents a significant gap in the research. As far as we are aware, no prior research has shown how well these additives work in graphite/LFP full cells, a cell architecture that is important to the commercial world. NMC cathodes have been shown to be able to intercalate sodium electrochemically with poor capacity retention, they also require sodium doping to improve reversible electrochemical intercalation of potassium, making NMC less directly compatible with sodium and potassium electrolyte additives[124], [125]. However, LFP have been demonstrated to reversibly intercalate sodium or potassium making them suitable candidates for cycling in mostly lithium electrolytes with sodium and potassium additives[126], [127]. Thus, by confirming the viability of NaPF_6 and KPF_6 additives in full-cell lithium-ion systems, our work closes a useful knowledge gap for both academia and industry applications and paves the way for future additive-based electrolyte designs that are compatible with battery chemistries relevant to the industry.

Chapter 3

Characterization methods

3.1 Physical Methods

3.1.1 Scanning electron microscopy (SEM)

An instrument used to directly study the structural development of active materials is scanning electron microscopy, or SEM[128]. Scanning electron microscopy (SEM) uses scattered and re-emitted electrons to create an image. The backscattered electrons or the secondary electrons released by the accessible atoms are detected when an electron beam is directed towards the sample. This method allow for examining morphological changes that occur during battery operation, including delamination, fracture development, and electrode volume expansion/shrinkage[129].

The SEM's fundamental working concept is the emission of electrons from an electron source, which produces a precisely focused beam of intense electrons. Usually, E_0 , the electron energy in this beam, is chosen between $E_0 = 0.1$ and 30 keV. Following emission from the source and high-energy acceleration, the electron beam is altered by apertures, magnetic and/or electrostatic lenses, and electromagnetism coils. These components work together to gradually decrease the beam's diameter and scan the focused beam in a raster (x-y) pattern, placing it successively at a number of distinct but closely spaced points on the specimen. Two outgoing electron products are produced at each of these distinct spots in the scan pattern as a result of the interaction between the specimen and the electron beam: (1) backscattered electrons (BSEs), which are beam electrons that, after being scattered and deflected by the electric fields of the atoms in the sample, come out of the specimen with a significant portion of their incident energy intact; as well as (2) secondary electrons (SEs), which are electrons that leave the specimen surface after being expelled from sample atoms by beam electrons. The secondary electrons have poor kinetic energy transfer and leave the specimen surface with very low kinetic energies, ranging from 0 to 50 eV, with the bulk of them being below 5 eV in energy, despite the beam

electrons usually being at high energy. These outgoing electron signals are detected at each beam point using one or more electron detectors, often a "dedicated backscattered electron detector" that is insensitive to SEs and an Everhart–Thornley "secondary electron" detector that is actually sensitive to both SEs and BSEs. The signal measured at each raster scan location on the sample is digitally recorded and stored in computer memory for each of these detectors. The signal is then used to determine the grey level at the corresponding X-Y location of a computer display screen, creating a single picture element (or pixel). To reduce the undesirable scattering that beam electrons, BSEs, and SEs would experience from coming into contact with atoms and molecules of ambient gases, the electron-optical column and specimen chamber in a standard vacuum SEM must function under high vacuum conditions ($<10^{-4}$ Pa) [130].

Figure 12 shows a diagram of a conventional SEM. The electronics console and the microscope column are the two main components. The objective lens, one or two condenser lenses, two pairs of beam deflection coils (scan coils for x, y deflection), the electron gun (which includes the cathode, Wehnelt cylinder, and anode), and apertures make up the microscope column. The cathode and Wehnelt cylinder produce the electron beams, which is then accelerated by the anode and directed toward the specimen via condenser lenses and deflection coils (x,y). Various detectors gather signals including CL, X-rays, backscattered electrons, and secondary electrons, which are then amplified and processed by the PC, monitor, and photo monitor. Although the contemporary FESEMs frequently have some kind of in-lens detectors, the specimen stage and detectors for the various signals produced by the electron–specimen interaction are positioned in the specimen chamber at the lower end of the microscope column. In order to fully utilize all of the information that SEM can offer, it is necessary to comprehend how it operates and how electron-beam parameters affect image resolution, contrast, signal intensity, and electron-specimen interaction [131].

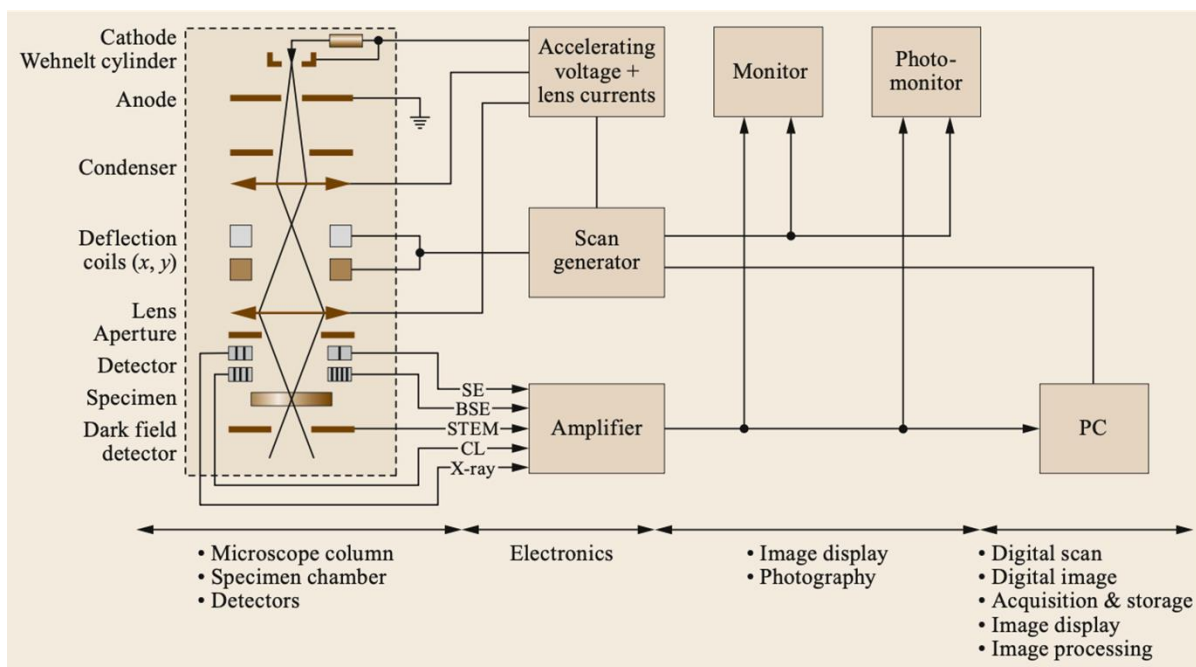


Figure 12 Schematic of a scanning electron microscope (SEM) showing key components and signal detection pathways [131]. Reprinted permission from [131]

In lithium-ion battery research, SEM plays a significant role in describing the morphology of electrode materials, tracking degradation mechanisms, and observing the creation and evolution of the solid electrolyte interphase (SEI)[132], [133].

In this study, graphite electrodes cycled with various electrolyte additions were seen on their surface using SEM. To get rid of any remaining electrolyte, samples were recovered in an inert atmosphere, then gently rinsed with dimethyl carbonate (DMC) and dried. Multiple magnifications were used to obtain the images in order to evaluate surface homogeneity, SEI morphology, and potential deterioration. SEM was conducted on a Tescan VEGA TS-5130 and an accelerating voltage of 20kV.

3.1.2 X-ray photoelectron spectroscopy (XPS)

The elemental content and corresponding chemical bonding of a material can be determined using a surface-analysis method called X-ray photoelectron spectroscopy (XPS). The photoelectron effect is

the basis for how this method works. When radiation (usually X-rays) is applied to samples, core-shell electrons are dislodged, causing a higher-valence electron to fall to a lower electron shell to fill the vacancy. As a result of this process, energy is released. The intensity of the released electron is intriguing since it is unaffected by the time or intensity of the incoming light. Instead, it depends on the energy of the incident photon. Electrons are gathered and their kinetic energy is measured after emission. The binding energy (in electron volts, or eV) serves as the foundation for determining the x-axis of the XPS plot. The resulting plot, which is plotted against intensity on the y-axis, can reveal details about the atom from which an electron originated, its valence shell (1s, 2p, etc.), and the environment the atom is in (e.g., a carbon bonded to a nitrogen vs. oxygen vs. phosphorous).

The penetrating power of these photons in a material is restricted to 1–10 micrometres. The measured kinetic energy of the released electrons is provided by:

Equation 1 $KE = h\nu - BE - \phi$

where BE is the binding energy of the atomic orbital from which the electron comes, $h\nu$ is the photon's energy, and ϕ is the spectrometer's work function. The concentration of the elements in the surface can be identified and ascertained using XPS since every element has a distinct set of binding energies. An electron spectrometer measures the kinetic energy of the electrons as they exit the sample. The analyzer often operates as an energy window, also known as the pass energy, and only accepts electrons with energies that fall inside this range. The pass energy is fixed in order to preserve a consistent energy resolution. Before entering the energy analyzer, incoming electrons are adjusted to the pass energy. A changeable electrostatic field is applied in front of the analyzer to enable scanning for various energies[134], [135].

For battery research and development, X-ray photoelectron spectroscopy (XPS) has emerged as one of the most significant and practical instruments, with an emphasis on electrodes and solid electrolyte

interphase (SEI) layers[136]. Using this method, scientists can find important SEI species such LiF, Li_2CO_3 , organic carbonates, phosphates, and byproducts of salt and solvent breakdown, as well as the existence of prominent C–F peaks[137], [138].

In this study, graphite anodes cycled in electrolytes containing LiPF_6 , NaPF_6 , and KPF_6 were examined for surface chemistry using XPS. Samples were taken out of cycled half-cells in a glovebox filled with argon, rinsed with dimethyl carbonate (DMC) to get rid of any remaining electrolyte, and then dried. The chemical states of the SEI were analyzed using survey and high-resolution scans, with particular attention to the Na 1s, F 1s, Li 1s, and C 1s regions. XPS was performed on a Thermofisher Scientific Nexsa G2 Surface analysis system with a monochromatic Al $K\alpha$.

3.2 Electrochemical methods

When assessing the stability, performance, and degrading behavior of lithium-ion battery systems, electrochemical characterization is essential. This work investigated capacity retention, solid electrolyte interphase (SEI) formation and interfacial resistance using a combination of galvanostatic charge–discharge, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS). In both half-cell and full-cell configurations, both methods offer complementary insights into how electrolyte additives affect the SEI.

3.2.1 Galvanostatic measurements

Tests known as Galvanostatic Charge/Discharge (GCD) or Constant Current Charging/Discharging are frequently used to assess energy storage devices such as batteries. In GCD, a material or system is charged and discharged within a predetermined potential limit by applying continuous positive and negative currents; this process is repeated for several cycles. Important details on electrode behavior, particular capacity, voltage plateaus, coulombic efficiency, and long-term cycle stability can be found in the resulting voltage–capacity (or voltage–time) profiles[139]. For example, the presence of flat

voltage plateaus may suggest clearly defined redox processes; electrode degradation may be indicated by a steady capacity decrease over cycles; and reversible lithium-ion transport and SEI stability may be confirmed by a high coulombic efficiency (e.g., >99%) over a large number of cycles. The applied current in a galvanostatic experiment is equivalent to a specified C-rate. C-rate, is a measurement of how rapidly a battery is charged or drained based on the battery or electrode rated capacity[140].

Using electrolytes containing LiPF₆, NaPF₆, and KPF₆ additives, galvanostatic cycling was utilized in this work to evaluate SEI formation and performance in both half-cells and full cells. Depending on the cell configuration, SEI formation was conducted at 0.1C and 1C based on the graphite electrode capacity for half-cells and based on the lithium iron phosphate electrode for full cells, followed by cycling at higher rates (e.g., 0.5C, 2C, 4C, and 6C). Lithium foil was used as reference to cycle the graphite anode in half-cells, whereas graphite and LFP were used in full cells. SEI behavior under various electrolyte conditions was quantified by extracting the specific capacity, irreversible capacity loss, and coulombic efficiency in the first cycle. Capacity retention over 50 cycles was assessed using long-term cycling data, which demonstrated the stability of SEI layers grown with the addition of the K⁺ and Na⁺ cations.

3.2.2 Cyclic voltammetry (CV)

In cyclic voltammetry, the potential applied to a working electrode is scanned between two predetermined potential values, and the current flow that results is monitored. The energetics of redox reactions, the kinetics and reversibility of electron transport, and the kinetics of associated chemical reactions are directly revealed by the current response. The oxidation and reduction of an electroactive species, which may be in solution or adsorbed at the electrode surface, are driven by the experimental cycling of a working electrode's potential between two potential limits. In a positive potential scan, an anodic current is derived from the oxidation of the species, whereas in a negative potential scan, all of

the species at the electrode interface are reduced and a cathodic current is recorded. Perhaps the most popular method for characterizing redox systems is cyclic voltammetry (CV). It can offer qualitative details regarding the quantity and stability of oxidation states[141], [142], [143]. Reversible lithium intercalation into graphite, for instance, may be indicated by clearly defined redox peaks in the CV profile, but greater resistance or deterioration of the SEI layer may be suggested by peak shifts or broadening over several cycles.

In order to assess the intercalation behavior and electrochemical stability in a range of electrolytes, CV measurements were carried out on both graphite anodes and LFP cathodes. Using Swagelok cells, the scans were carried out at a rate of 0.05 mV/s in the voltage range of 2.6–3.6 V for full cells and 0.01–2.0 V vs. Li/Li⁺ for graphite half-cells. The obtained voltammograms were utilized to assess the reversibility of lithium intercalation across the various electrolyte systems and to confirm whether Na⁺ or K⁺ ions intercalate into the electrode structure. It was possible to determine if added species were experiencing plating or side reactions on the electrode surface by looking for anodic/cathodic peaks in particular voltage regions.

3.2.3 Electrochemical impedance spectroscopy (EIS)

EIS, or electrochemical impedance spectroscopy, is an effective and popular non-invasive technique for characterizing LIBs[144]. Throughout a battery's life, EIS can be utilized as a non-destructive method for diagnostic or predictive purposes. Usually, the measurement method involves delivering a sinusoidal voltage or current with specific frequency and amplitude, then measuring the output voltage or current's amplitude and phase shift, respectively. To create a complex impedance spectrum, this process is done for a variety of frequencies, usually in the kHz to mHz range. This makes it feasible to investigate energy storage mechanisms with various time constants. The impedance, capacitance, and inductance of the various cell components and processes can be probed, and show as distinct features

on the resulting Nyquist plot (which plots the imaginary part of the impedance against the real part) and/or Bode plot (which plots either magnitude and phase or real and imaginary parts as a function of frequency).

An idealized Nyquist plot for a commercial LIB is displayed in Fig. 13. The inductive behavior seen in the spectrum's upper frequency range may be caused by the geometry of the cell and its windings, or it may be an artifact of the measurement system (the wires that connect the cell to the measuring equipment).

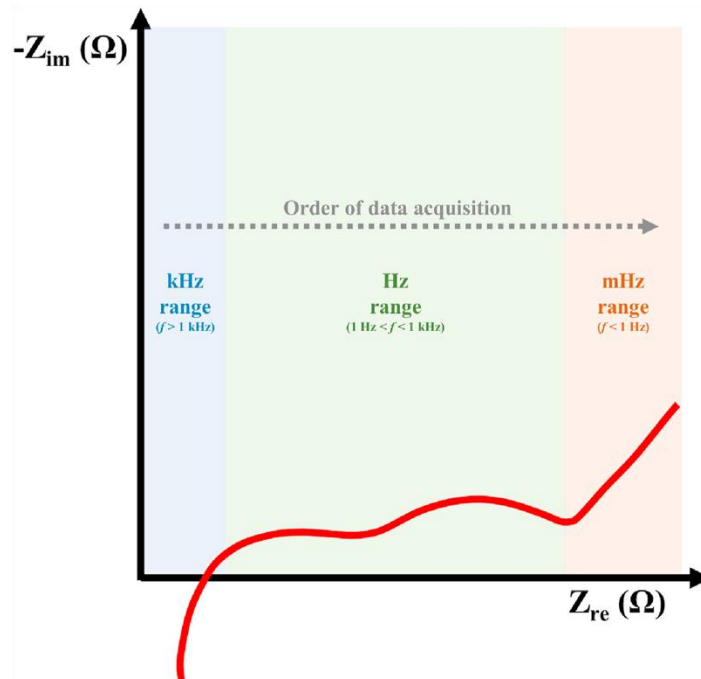


Figure 13 An example of a Li-ion cell EIS measurement displayed graphically in a complex impedance plot (also known as a Nyquist plot) [145]. Reprinted permission from [145], (open access) <https://creativecommons.org/licenses/by/4.0/>

When the inductance effect is appropriately eliminated, the high-frequency intercept with the real axis equals the sum of the internal ohmic resistances of the electrolyte, active material, current collectors, and electrical (metallic) connections. The electrochemical reactions taking place at the

electrode/electrolyte interfaces inside the cell, which combine resistive and capacitive effects, semi-circles the main cause of the arcs that emerge in the mid-frequency region. Lithium transport across the solid electrolyte interphase (SEI) and lithium (de-)intercalation at each electrode take place concurrently with dielectric polarization and double layer (dis)charging, respectively. Because of this, at least four distinct processes contribute (anode charge transfer, anode SEI, cathode charge transfer, and cathode SEI). The low-frequency tail in commercial cells mostly represents the diffusion of solid state lithium ions in the cell electrodes' active material[145], [146], [147], [148], [149].

In this study, graphite electrodes cycled in electrolytes containing LiPF_6 , NaPF_6 , and KPF_6 were compared for interfacial impedance using EIS. Before and after the SEI formation cycle, measurements were made using symmetric cells.

Chapter 4

Facile SEI improvement in the artificial graphite/LFP Li-ion system: via NaPF₆ and KPF₆ electrolyte additives

4.1 Introduction and purpose of the study

As mentioned, lithium-ion batteries have garnered significant attention over the past few decades. Over the past 30 years, the applications for these rechargeable, lightweight, and effective batteries have grown significantly. From our phones, computers, and video cameras to electric vehicles [150]. However, when it comes to electric vehicle batteries, higher energy density, long cycle performance, lower production costs, and fast charging features are still needed [151].

The SEI is essential because it permits lithium-ion transport while halting ongoing electrolyte degradation; however, if it is thick or resistive, it hinders stability and power delivery[152]. It has been shown that electrolyte additives can effectively fine-tune the SEI, improving interfacial ion transport and lowering irreversible capacity loss[153]. Common additives such as lithium bis(oxalate)borate (LiBOB), vinylene carbonate (VC), and fluoroethylene carbonate (FEC) provide LiF-rich protective coatings that increase cycling durability and SEI conductivity[154].

As far as we know there are no studies demonstrating the effects of sodium and potassium additives in a full cell system. This is a fundamental research gap as the popular NMC is not compatible with these additives. NMC cathodes have been shown to be able to intercalate sodium electrochemically with poor capacity retention, they also require sodium doping to improve reversible electrochemical intercalation of potassium, making NMC less directly compatible with sodium and potassium electrolyte additives[155], [156]. However, lithium iron phosphate (LFP) is compatible with both. Lithium Iron Phosphate (LFP), on the other hand, is one of the main choices for EV batteries due to its low cost of

raw materials, low toxicity, environmentally friendly nature, excellent safety properties, cycling performances, and long cycle life, making it a promising candidate for next-generation advanced high-energy lithium-ion batteries [157]. LFP have been demonstrated to reversibly intercalate sodium or potassium making them suitable candidates for cycling in mostly lithium electrolytes with sodium and potassium additives[158], [159]. Additionally, compared to chemistries based on nickel and cobalt, LFP cathodes are safer for demanding applications because to their greater thermal stability and resistance to thermal runaway under short-circuit and abuse circumstances[160].

Other than utilizing electrolyte additives, another approach would be to form the SEI at different C-rates. It has been shown that by controlling the SEI formation at high current densities, the charging time of the graphite anode may be greatly reduced [161], [162]. Rangom et al. demonstrated that when compared to the SEI layer formed at 100 C, the SEI layer formed at the current density used in the industry, which is 0.1 C, decreases the overall Li^+ diffusivity by at least 23% [163].

Our goal in this work is to use sodium and potassium electrolyte additives to successfully and scalably form a solid electrolyte interphase (SEI) layer in graphite/LFP full cells. The main objective is to assess the effects of these additives on cycling performance and SEI formation in both full-cell and half-cell setups. We predict that the addition of potassium and sodium ions will change the interfacial behavior and SEI composition on graphite electrodes, improving performance metrics and lowering irreversible capacity loss. The ultimate goal of this research is to learn more about how mixed-ion electrolytes impact the interface between electrode and electrolyte materials, which will help design next-generation lithium-ion batteries.

4.2 Experimental methods

4.2.1 Materials

The base electrolyte solution was bought from Sigma-Aldrich and contained 1M LiPF₆ in a 1:1 (v/v) mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC). Sodium hexafluorophosphate (NaPF₆), Potassium hexafluorophosphate (KPF₆), and Lithium hexafluorophosphate (LiPF₆) salts were also obtained from Sigma-Aldrich. Lithium Iron Phosphate (LFP) electrodes and single-sided artificial graphite electrode sheets on Cu were purchased from the NEI Corporation with a loading mass of 7.32 mg/cm² and 5.22 mg/cm² respectively. Also, glass microfiber separators were acquired from Whatman.

4.2.2 Electrode and electrolyte preparation

Electrode and electrolyte preparation: Four formulations of the electrolyte were made. There was 1.22M LiPF₆ in sample 1 (control). Sample 2 included 0.22M NaPF₆ and 1M LiPF₆. In Sample 3, there was 0.22M KPF₆ and 1M LiPF₆. In Sample 4, there was 0.02M KPF₆ and 1M LiPF₆. Table 1 summarizes the electrolyte formulations. A glove box filled with argon (H₂O and O₂ < 0.8 ppm) was used to weigh and dissolve the extra salts in the base electrolyte. This was done to avoid moisture contamination. For cell assembly, the produced electrolytes were utilized right away. The schematic of the Swagelok cell configuration used in this study is shown in Figure 14.

Table 1 Electrolyte formulations used in this study

Sample No.	Electrolyte composition
Sample 1 (Control)	1.22M LiPF ₆
Sample 2	1M LiPF ₆ + 0.22M NaPF ₆
Sample 3	1M LiPF ₆ + 0.22M KPF ₆
Sample 4	1M LiPF ₆ + 0.02M KPF ₆

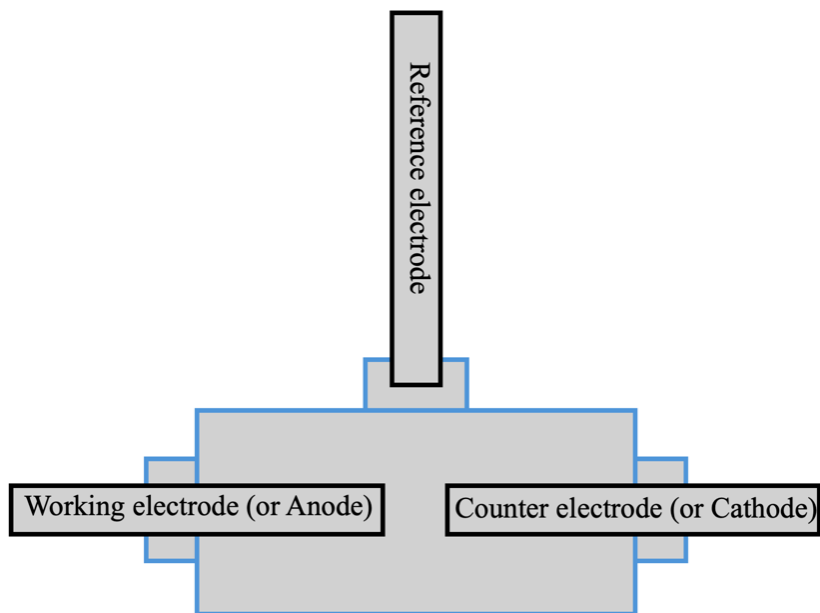


Figure 14 Schematic of the Swagelok-type cell configuration employed in this study.

4.2.3 Characterization

X-ray photoelectron spectroscopy (XPS) was utilized to analyze the surface chemistry and chemical composition of SEIs formed on graphite electrodes with regard to different electrolyte additives. XPS was performed on a Thermofisher Scientific Nexsa G2 Surface analysis system with a monochromatic Al K α . EIS was done on Biologic SP-150 instrument. SEM was conducted on a Tescan VEGA TS-5130 and an accelerating voltage of 20kV.

4.2.4 Electrochemical methods

Swagelok cells were assembled in an Argon-filled glove box with O₂ and H₂O below 0.8 ppm. Using Biologic's SP-150 galvanostatic charge/discharge cycling, studies were performed in the potential range of 2.6V to 3.6 V versus Li/Li⁺ for full cells, and 2V to 0.02V for half cells. The formation of SEI layers occurred at C-rates of 0.1 C and 1 C, respectively. Cycling tests were performed at 2 C, 4 C, and 6 C for half cells and 0.5C for full cells. Moreover, The CV experiment was carried out for both anode (from 2V to 0.02V) and cathode (from 2.7V to 4.2V) at a scan rate of 0.05 mVs⁻¹. Symmetric graphite

cells were used for EIS measurements. The measurements were made between 1 MHz and 0.1 Hz at open-circuit voltage with an amplitude of 10 mV AC.

4.3 Results and discussion

The initial lithiation curves, which corresponds to the SEI formation of all three electrolytes, are illustrated in Figure 15 (c). The control cell, with 1.22M LiPF₆, achieves a specific capacity of 607 mA·h/g following SEI formation, with an initial coulombic efficiency of 70.84% and an irreversible capacity of 177 mA·h/g. In contrast, the cells with NaPF₆ and KPF₆ additives yield lower specific capacities of 520 mA·h/g and 517 mA·h/g, respectively. However, these additives show enhanced initial coulombic efficiencies, with NaPF₆ reaching 79.23% and KPF₆ reaching 78.72%, corresponding to lower irreversible capacities of 108 mAh g⁻¹ and 110 mAh g⁻¹ respectively. Less specific capacity during first lithiation shows less SEI has been formed on the anode material, resulting in a likely thinner SEI layer but less irreversible loss of lithium. In order to better understand the effect of electrolyte additives on the battery performance, cycle rate and CV experiments have been conducted.

The cyclic voltammetry (CV) profiles for both LFP cathode and graphite anodes conducted at a sweep rate of 0.05 mV/s are presented in figure 15 (a) and (b). Characteristic peaks corresponding to the staging phenomena during lithium intercalation and deintercalation can be seen in these graphs. For the graphite anodes, as illustrated in the figure 15 (a), all three electrolyte additives show peak currents at about 0.2 V, according to the anodic scans for the graphite anode. This finding implies that the intercalation potentials for the various electrolyte additions is not significantly altered. However, during the cathodic scan, a little shift in the presence of the NaPF₆ additive can be seen, but it's negligible. Additionally, potassium plating is observed for the electrolyte added with 0.22M KPF₆. However, no evidence of potassium plating can be found in the electrolyte with 0.02M KPF₆. This can happen to multiple reasons. For instance, at lower concentrations of KPF₆ the deposition potential of potassium

is relatively low. This means that the graphite anode does not reach the necessary potential for potassium to deposit as metal during regular cycling, especially at lower electrolyte concentrations. In contrast, higher concentrations of KPF_6 result in higher deposition potentials, making it easier for the anode potential to reach these values during cycling, thus triggering potassium deposition. Moreover, at lower concentrations, there are fewer potassium ions available to participate in the deposition process. This reduces the likelihood of reaching the conditions necessary for potassium plating. Another reason for this would be that, at lower concentrations, the presence of K^+ ions allow the battery to operate normally without significant polarization or resistance build-up. Higher concentrations, however, may cause the bigger K^+ ions to impede the flow of Li^+ ions, increasing internal resistance and changing the anode potential. Potassium plating may be made easier by this shift, which may bring the anode potential closer to the potassium deposition potential[164] .

According to the LFP cathode CV curves (figure 15(b)), it appears that the peaks for the control cell with 1.22M LiPF_6 and electrolytes with KPF_6 additives all occur at the same voltage, which corresponds to no intercalation of KPF_6 . However, the results indicate that the NaPF_6 additive has a slight shift for both anodic and cathodic scan. This suggests that sodium ions intercalate and deintercalate into and out of the LFP structure. However, the use of NaPF_6 as an electrolyte additive result in increased polarization, as evidenced by the shift. Specifically, during the cathodic scan, the potential of NaPF_6 -added cell increases from 3.8V (observed with both LiPF_6 and KPF_6 additives) to 3.9V, and during the anodic scan, decreases from approximately 3V to slightly below 3V. This increased polarization indicates a larger voltage difference between lithiation and delithiation processes, which could negatively impact the energy efficiency of the cell. Thus, using NaPF_6 as an electrolyte additive would make a slight negative impact on the energy efficiency of the battery. It is crucial to recognize that thermodynamic irreversibility and entropy formation have a substantial impact on ion transport

behaviour in electrochemical systems, even though in-depth b-value or scan-rate-dependent investigations were outside the purview of this study. This is especially important in mixed-ion environments, such as the one Li et al. examined in their study of entropy and ion dynamics in supercapacitor systems[165].

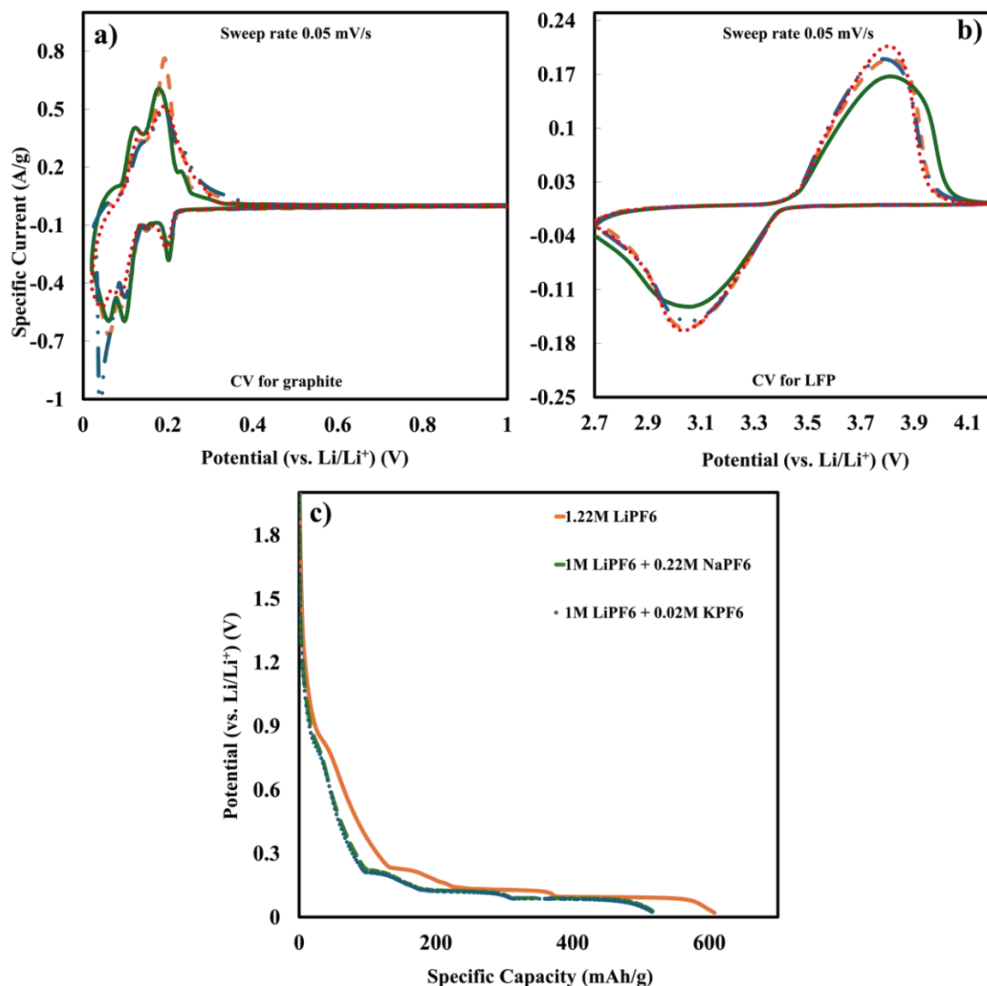


Figure 15 Cyclic voltammetry (CV) curves of (a) the graphite anode, (dashed orange: 1.22M LiPF₆), (green line: 1M LiPF₆+0.22M NaPF₆), (dashed and dotted dark blue: 1M LiPF₆)0.22M KPF₆), and (dotted red: 1M LiPF₆+0.02M KPF₆) and (b) the LFP cathode, highlighting electrochemical behavior in deferent electrolyte formulations (sweep rate – 0.05 mV/s), and initial lithiation curves of three electrolyte additives, control LiPF₆ (orange), NaPF₆ (green), and (0.02M) KPF₆ (dotted blue) (c)

Figure 16 (a) and figure 17 provide details about cycle rate of control LiPF₆, NaPF₆-added sample, and 0.02M KPF₆ additives half cells with the formation of SEI at 0.1C (figure 16(a)) and 1C (figure 17) over various C-rates. The capacity is normalized to the 10th cycle. It can be seen from figure 16 (a) that, when the SEI is formed at 0.1C, the control cell with LiPF₆ shows a superior performance in terms of capacity across the various C-rates, specially at 4C and 6C. The SEI formed in samples with NaPF₆ and KPF₆ additives exhibits higher resistance. However, figure 17 reveals that, this resistance is gone if the SEI is done at 1C. The stability of the cells is also improved when they return to lower C-rates when NaPF₆ and KPF₆ is added to the electrolyte (4C-r, 2C-r, 1C-r). The Coulombic efficiency for the three electrolytes during 70 cycles at different C-rates is shown in Figure 16(b). Throughout the experiment, every cell maintained a high Coulombic efficiency, staying above 99%, suggesting robust cycling performance and little adverse effects. Nevertheless, during the high-rate 6C cycle and the ensuing 4C-return phase, the cell with 0.02M KPF₆ additive displayed a discernible decrease in Coulombic efficiency, most likely as a result of enhanced polarization or unstable SEI behaviour at high current densities. The efficiency notably improved in the later phases, indicating that the SEI created under high-rate cycling conditions somewhat stabilized. Figure 16 (c) represents the EIS data for cells with and without SEI formed at 0.1C. The equivalent circuit model $R_1 + (Q_2 \parallel R_2) + (Q_3 \parallel R_3) + Q_4$ that was utilized to fit the EIS data is shown in figure 16 (d). R_1 represent ion impedance in the solvent, Q_2/R_2 represent electronic interface and is fitted to the high frequency part of the elongated semi-circle, while Q_3/R_3 represents ion interface and is fitted to the lower frequency part of the semi-circle. Constant phase element Q_4 represents the overall capacitance of these symmetric capacitor test cells. Among the samples with SEI formed at 0.1C, the control sample with 1.22M LiPF₆ shows the highest solution impedance (R_1) (2.41 $\Omega \cdot \text{cm}^2$). However, the cell with 1M LiPF₆ and 0.22M NaPF₆ shows the lowest impedance at the low to mid impedance range (2.01 $\Omega \cdot \text{cm}^2$). This suggests that the addition of NaPF₆ enhances the SEI formation. However, the sample with 1.22M LiPF₆ and 0.02M

KPF₆ shows slightly higher impedance (2.13 Ω·cm²) compared to the NaPF₆ added sample. The ionic conductivity of the electrolytes was barely affected by the addition of NaPF₆ and KPF₆ additives, as shown by the impedance spectra of samples without SEI formation in Figure 16 (c). In the case of the control electrolyte with LiPF₆, the extracted solution resistance (R_s) values were 2.10 Ω·cm², 1.94 Ω·cm² for the electrolyte that had NaPF₆ added, and 2.09 Ω·cm² for the electrolyte that had KPF₆ added. These slight variations—within around ±4%—indicate that the enhancements in electrochemical performance are caused mainly by these additives' effects on SEI characteristics rather than modifications in ionic conductivity. The ion interface level (Q₃ and R₃) showed notable changes, confirming the claim that SEI formation alters this area in particular. With values more than doubling in the case of LiPF₆, R₃ shows a significant rise. This rise is in line with the extra ionic transport resistance at the interface caused by a resistive SEI layer. The electrochemical signature of SEI formation—a more resistive, less capacitive interface, which is a feature of passivating SEI films—is further supported by the notable decrease in Q₃ and the rise in R₃.

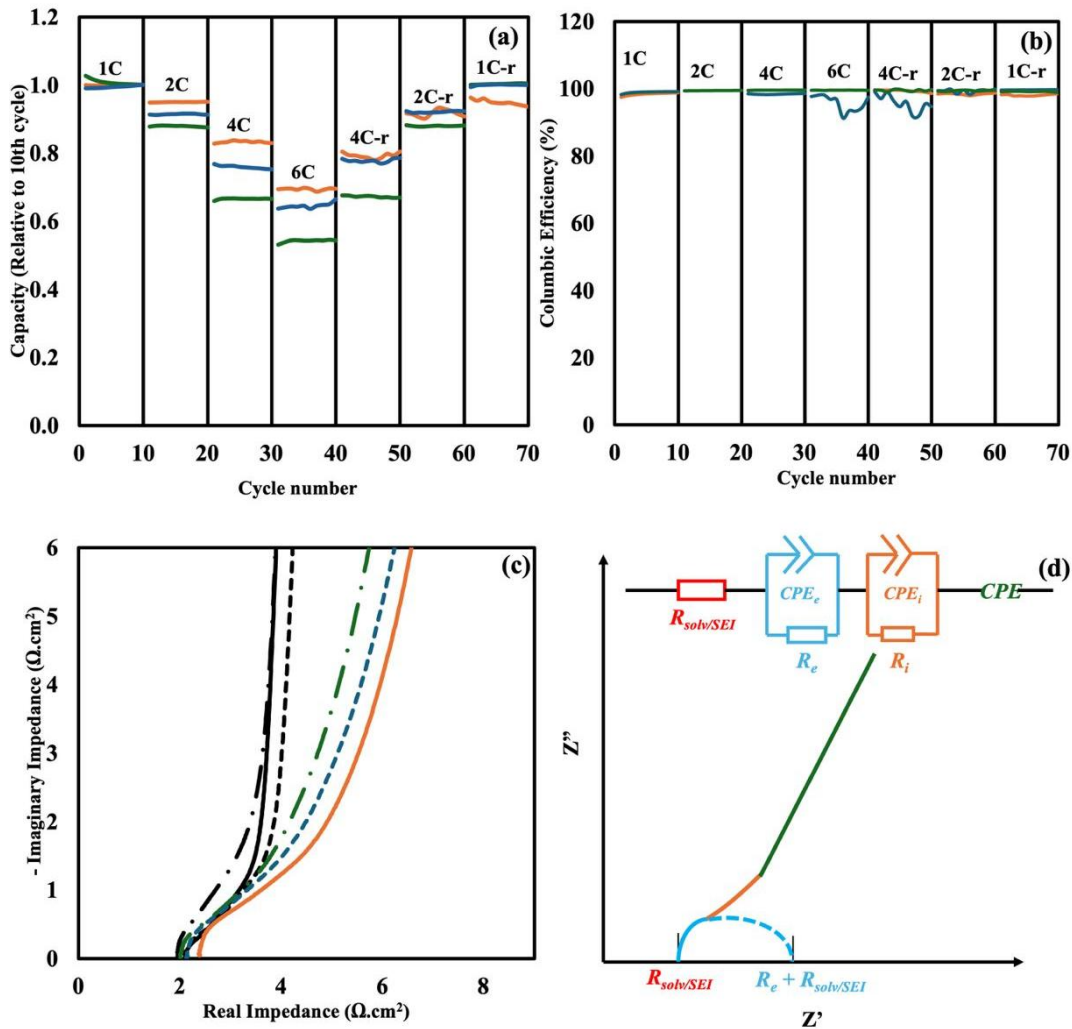


Figure 16 Cycle rate performance of half-cells with three different electrolytes, 1.22M LiPF6 (orange), 1M LiPF6+0.22M NaPF6 (green), and 1M LiPF6+0.02M KPF6 (blue) - SEI formed at 0.1C (a) columbic efficiency of graphite half-cells cycled at different C-rates, which correlates to the capacity retention data displayed in figure 15 (a) and EIS data for cells with and without SEI formed at 0.1C – (orange line: 1.22M LiPF6 with SEI at 0.1C), (dashed and dotted line: 1M LiPF6+0.22M NaPF6 with SEI at 0.1C), (dashed dark blue: 1M LiPF6+0.02M KPF6 with SEI at 0.1C), (black line: 1.22M LiPF6 without SEI), (black dashed and dotted: 1M LiPF6+0.22M NaPF6 without SEI), and (black dashed line: 1M LiPF6+0.02M KPF6 without SEI) (c), two parallel combinations of constant phase elements and resistances that reflect interfacial processes, and a series resistance make up the equivalent circuit model that was utilized to match the EIS data (d)

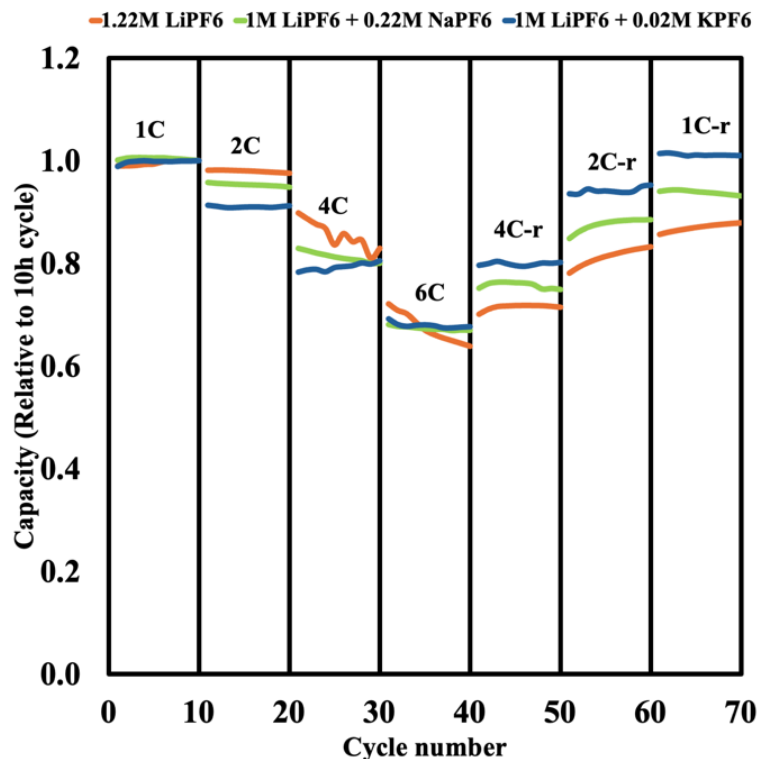


Figure 17 Cycle rate performance of half-cells with three different electrolytes, 1.22 M LiPF₆ (orange), 1 M LiPF₆ + 0.22 M NaPF₆ (green), and 1 M LiPF₆ + 0.02 M KPF₆ (blue) - SEI formed at 0.1 C.

Using the same electrolyte compositions, full cells were assembled and cycled for 50 cycles at 0.5C between 2.6V and 3.6V after the electrolyte effects were confirmed in half-cell experiments (figure 18(a)). Although LFP had an initial loading of 1.25 mAh/cm², different electrolytes had different measured capacities following SEI formation because of differing levels of irreversible capacity loss (ICL). According to figure 18(a), After SEI formation, the capacity decreased to 0.69 mAh/cm², and the 1.22 M LiPF₆ electrolyte showed the highest ICL (44.8%). By comparison, the electrolyte containing 1 M LiPF₆ + 0.22 M NaPF₆ had the lowest ICL (33.6%) and retained 0.83 mAh/cm², whereas

the electrolyte containing 1 M LiPF₆ + 0.02 M KPF₆ had an intermediate ICL (37.6%) and a capacity of 0.78 mAh/cm².

The trends in capacity retention further deviated over the first 50 cycles. By the 50th cycle, the LiPF₆ electrolyte's capacity had dropped to 0.32 mAh/cm², indicating severe degradation. On the other hand, the electrolyte containing KPF₆ demonstrated a moderate capacity retention of 0.47 mAh/cm², whereas the electrolyte with NaPF₆ maintained the maximum capacity at 0.67 mAh/cm². According to these findings, NaPF₆ and KPF₆ improve long-term cycling performance by reducing irreversible capacity loss and reducing SEI formation. Our previous half-cell results, which showed that NaPF₆ and KPF₆ affected SEI composition and interfacial stability, are consistent with the full-cell data. Lower capacity retention and higher lithium consumption are the outcomes of the baseline LiPF₆ electrolyte's facilitation of larger SEI formation. Compared to LiPF₆, KPF₆ reduces initial capacity loss; nevertheless, it is less effective over the long term than NaPF₆. In addition to the capacity data in figure 18 (a), figure 18 (b) shows the Coulombic efficiency of the full cells across 50 cycles. With values remaining close to 99% during the cycle, all three electrolyte systems demonstrated continuously high Coulombic efficiency, indicating low parasitic reactions and good reversibility of the charge-discharge processes in all formulations. Additional tests were carried out utilizing sophisticated electrodes that could generate SEI at greater current densities in order to confirm the effectiveness of the NaPF₆ and KPF₆ additives. These studies demonstrate that, under both 1C and 0.1C SEI formation circumstances, NaPF₆ consistently provides improved capacity retention when compared to the baseline and KPF₆-containing electrolytes, as illustrated in figure 19(a) and figure 19(b). Interestingly, under 1C formation circumstances, NaPF₆ inhibited lithium plating, whereas the baseline electrolyte showed early indications of plating. These results support NaPF₆'s ability to stabilize SEI and improve long-term

cycling performance, particularly when fast-formation methods and high-conductivity electrode designs are used.

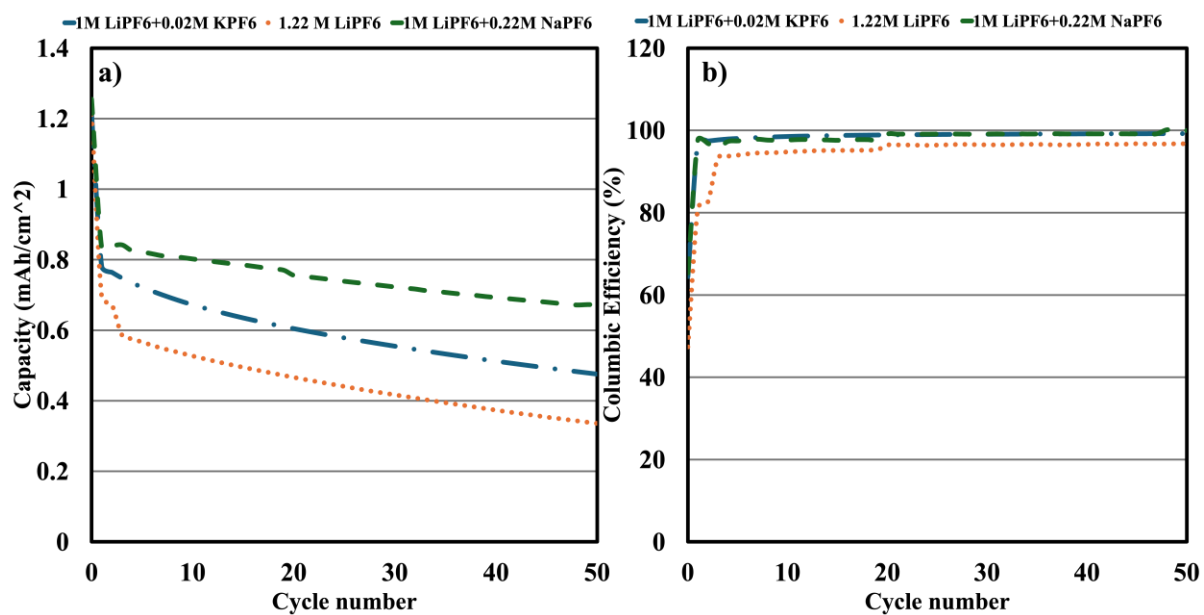


Figure 18 Cycle rate performance of full cells including 1.22M LiPF6 (orange), 1M LiPF6+0.22M NaPF6 (green), and 1M LiPF6+0.02M KPF6 (blue) at 0.5C after SEI formation at 0.1C for 50 cycles (a), columbic efficiency of the full cells over 50 cycles (b)

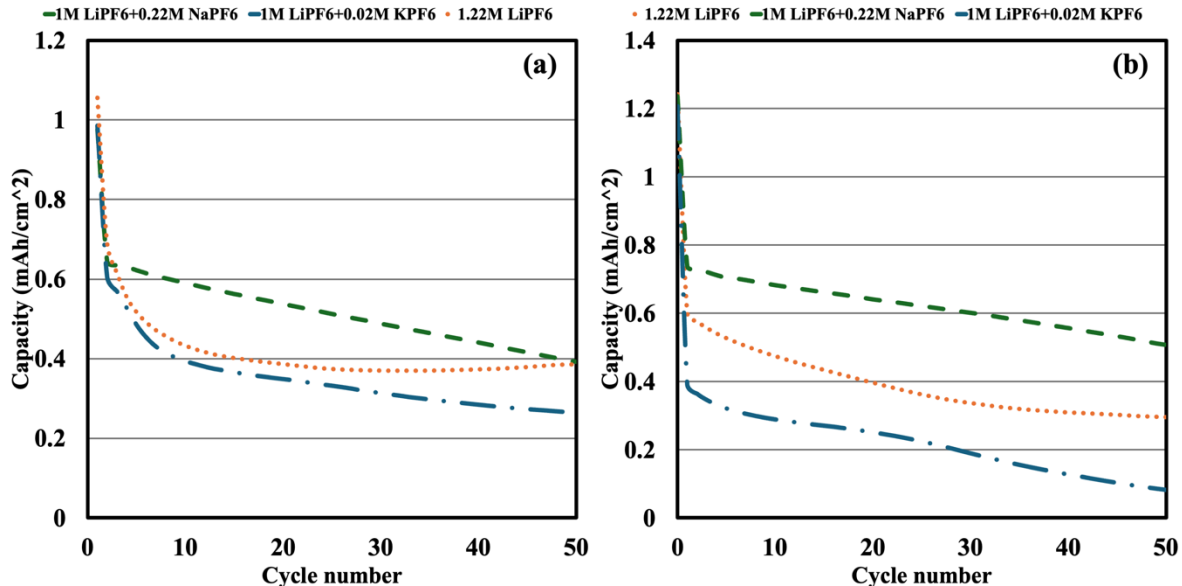


Figure 19 Cycling performance of full cells with three different electrolytes, 1.22 M LiPF₆ (orange dotted line), 1 M LiPF₆ + 0.22 M NaPF₆ (dashed green line), and 1 M LiPF₆ + 0.02 M KPF₆ (dashed and dotted blue line) with SEI formed at 1C using advanced electrodes (a) and cycling performance of the cells with advanced electrodes with SEI formed at 0.1 C

XPS was carried out on the graphite anodes in order to examine the surface chemistry of the solid electrolyte interphase (SEI) that forms in various electrolyte systems. The presence and impact of Na and K in the SEI were verified by high-resolution scans for Na 1s, F 1s, Li 1s, and C 1s on three separate samples. To verify sodium incorporation in the SEI for the NaPF₆-containing electrolyte (sample 2), the Na 1s scan (Figure 20 (c)) was employed. Successful sodium incorporation was demonstrated when NaPF₆ was added to the electrolyte since sample 2 had a noticeable Na peak at 1072 eV, whereas the control sample (1.22M LiPF₆) did not exhibit it.

High-resolution F 1s, Li 1s, and C 1s scans were performed on sample 1 (control) and sample 4 (1M LiPF₆ + 0.02M KPF₆) in order to assess the role of Potassium to SEI formation. Figure 20 (a) and (b) show the F 1s spectrum for sample 1 and 4. The C-F bond contribution increased from 10.09% in the control sample to 12.79% in sample 4, indicating that K affects surface species associated to fluorine.

Additionally, the Li 1s spectrum, which is depicted in figure 21 (a) and (b), provides additional evidence that K promotes LiF formation in the SEI by demonstrating a notable rise in LiF content, which increased from 19.78% in the control sample to 47.61% in sample 4. The observed trend in F 1s was further supported by the C 1s spectra (figure 21 (c) and (d)), which likewise shows an increase in C-F bonding, going from 10.84% in the control sample to 15.35% in sample 4. These findings align with previous literature that suggests K^+ may not exist as free K-containing species, but instead contribute mainly to the production of LiF and C-F bonds[166], [167]. The surface morphology of graphite anodes after SEI formation was examined by SEM (Figure 22). All electrolyte formulations produced similar SEI features, with no significant differences observed among the samples.

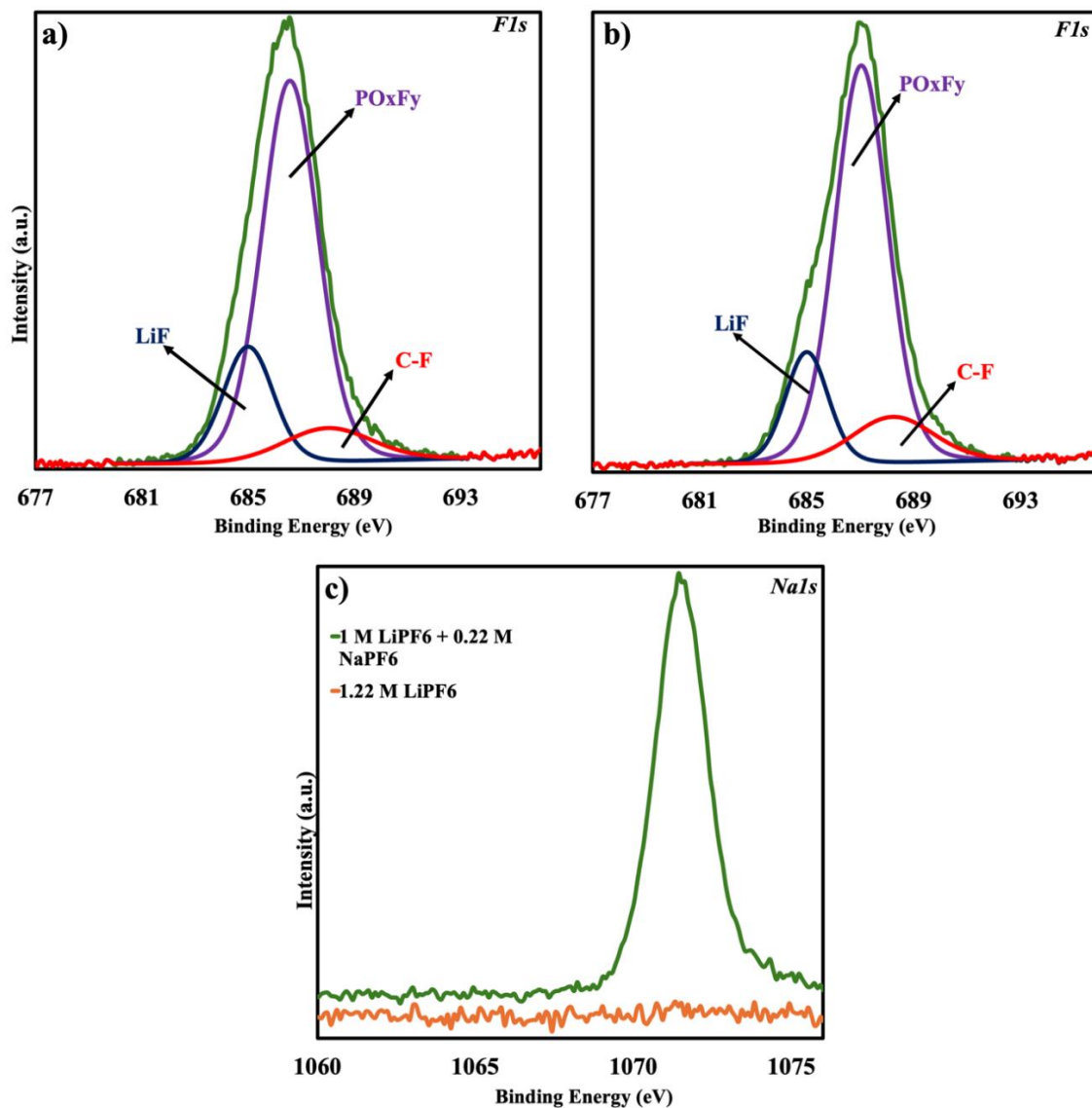


Figure 20 XPS F 1s spectra for control sample 1 (1.22M LiPF6) (a) compared with sample 4 (1M LiPF6+0.02M KPF6) (b), Na 1s spectra for sample 2 (1M LiPF6+0.22M NaPF6) compared with the control sample (c)

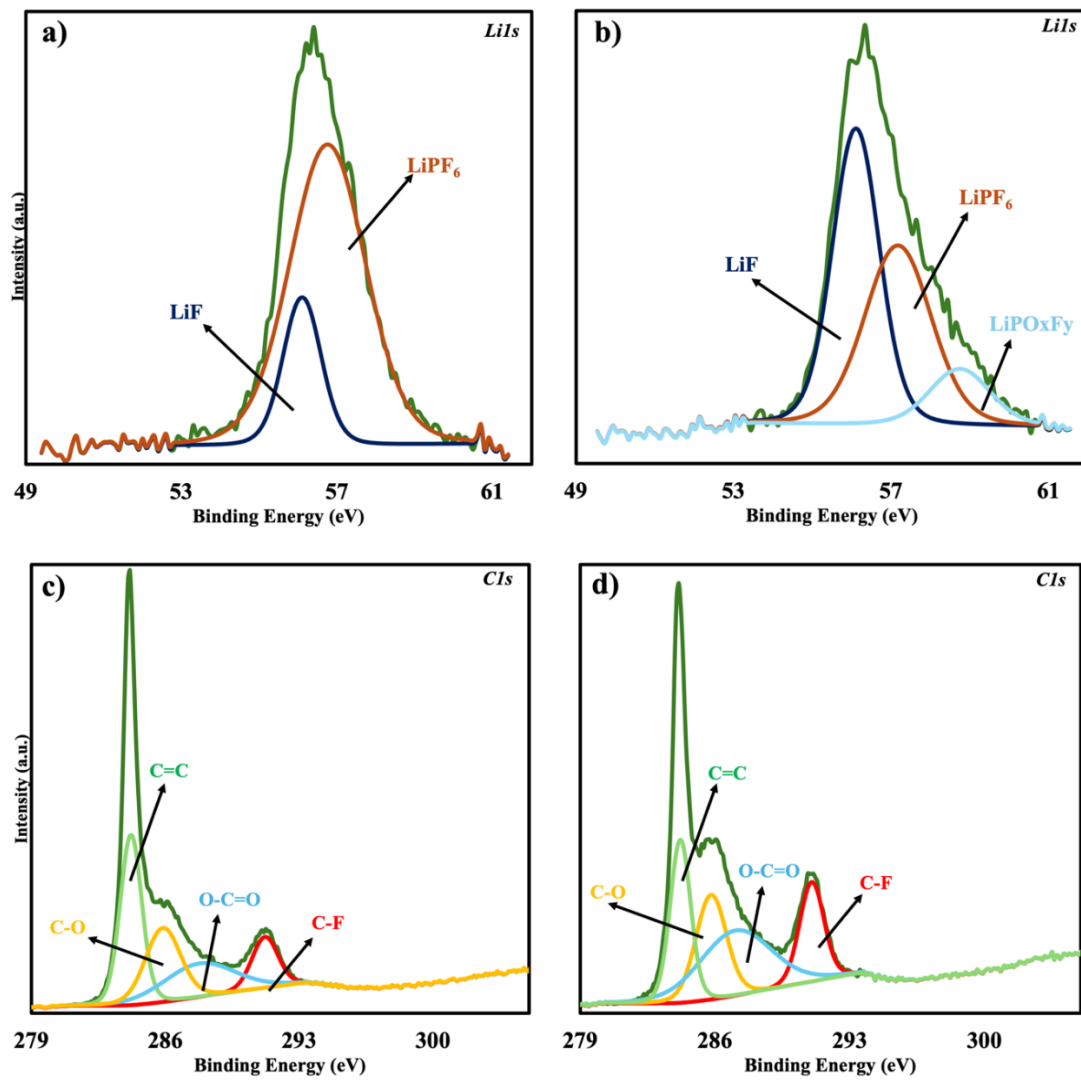


Figure 21 XPS spectra of Li 1s (a,b) and C 1s (c,d) for sample 1 (a,c) and sample 4 (b,d), showing SEI composition.

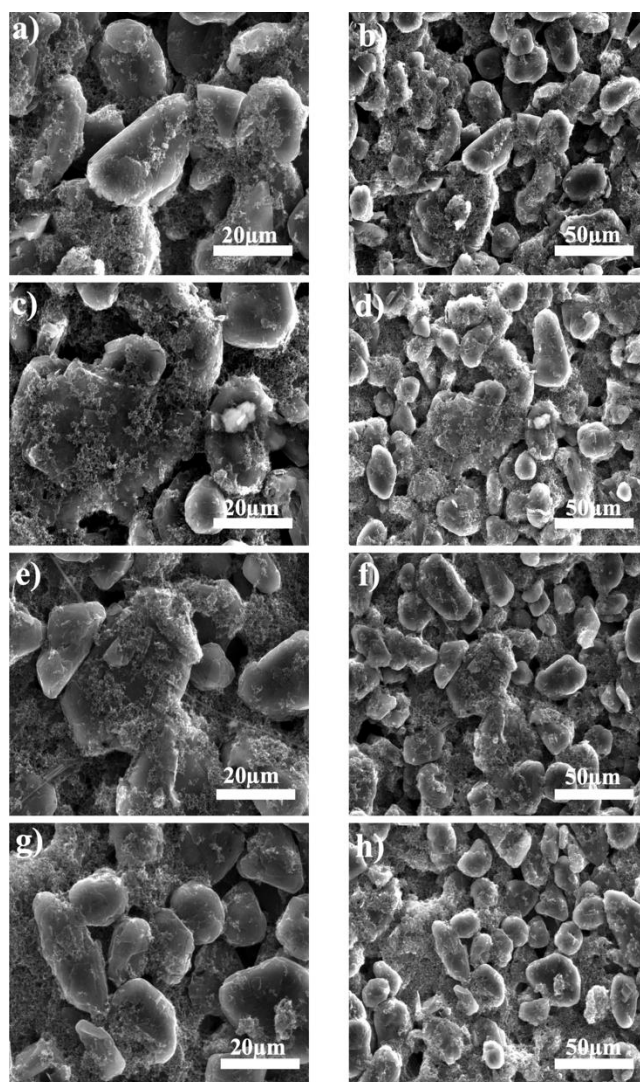


Figure 22 SEM images of graphite anodes after the formation of SEI at 0.1 C at 20 μm and 50 μm scales. Sample 1 (a) and (b), sample 2 (c) and (d), sample 3 (e) and (f), and sample 4 (g) and (h). All images were captured using an accelerating voltage of 20 kV.

4.4 Conclusion

This study shows that, in comparison to the conventional LiPF_6 electrolyte, relatively inexpensive and easy and straightforward to implement in an industry setting, NaPF_6 and KPF_6 electrolyte additives significantly decrease irreversible capacity loss and enhance capacity retention.

Key accomplishments:

- Irreversible capacity loss was significantly reduced by 38.98% and 37.85%, respectively, when KPF_6 and NaPF_6 were incorporated into graphite half-cells.
- In the graphite/LFP full cell system, the presence of KPF_6 and NaPF_6 significantly enhanced reversible capacity by limiting lithium consumption during SEI formation.
- The electrolyte with KPF_6 showed a 30.43% improvement, while NaPF_6 retained 67.39% more capacity than the baseline LiPF_6 after 20 cycles.

These findings demonstrate that NaPF_6 and KPF_6 additives can reduce capacity loss. Furthermore, KPF_6 lowers early capacity loss but is less efficient than NaPF_6 .

Furthermore, we showed that optimizing SEI formation at higher C-rates (1C), using high electrical conductivity electrodes, further increases the gains in initial coulombic efficiency obtained at 0.1C and shortens charging times without sacrificing SEI stability. Therefore, further research is warranted as SEI formed at 1C also further decreased SEI resistance in cells treated with KPF_6 and NaPF_6 additives compared to the ordinary reference LiPF_6 electrolyte. Future research will concentrate on creating electrode materials and electrolyte formulations that allow for stable SEI formation at high C-rates, to improve the lifespan and performance of fast-charging lithium-ion batteries.

Chapter 5

Summary and future work

This study investigated the effects of potassium (KPF_6) and sodium (NaPF_6) salt additions on the growth of solid electrolyte interphase (SEI) and cycle efficiency in graphite/LFP full-cell and half-cell systems. The irreversible capacity loss during early SEI creation and the degradation of battery performance after extended cycling were the two continuing issues in LIB development that were the subject of this study. Stable SEI layers and low lithium loss are essential for long-term operation and fast-charging feasibility in high-performance applications like electric vehicles (EVs), so these concerns are especially pertinent.

The study showed that adding KPF_6 and NaPF_6 additions to the standard LiPF_6 electrolyte formulation could enhance overall capacity retention and lower irreversible capacity loss. Irreversible capacity loss was decreased by roughly 39% and 38% for KPF_6 and NaPF_6 , respectively, in half-cell testing. After 20 cycles, full-cell cycling showed that cells based on KPF_6 improved by 30.43%, whereas cells based on NaPF_6 retained 67.39% greater capacity than the baseline electrolyte. These enhancements show that Na^+ and K^+ ions can control the interfacial processes that occur during SEI formation, improving the anode interface's electrochemical stability and reducing irreversible cation consumption.

Direct proof that these additives contribute to the SEI structure was provided by X-ray photoelectron spectroscopy (XPS), which verified the chemical incorporation of Na^+ and K^+ into the SEI layer. Furthermore, as all samples showed similar solution resistance values (within $\pm 3\%$), electrochemical impedance spectroscopy (EIS) demonstrated that the additions had no detrimental effect on the electrolyte's ionic conductivity. Further EIS analysis revealed that the samples with NaPF_6 added had

the lowest charge transfer resistance, indicating that a more stable and conductive SEI was created in their presence.

In addition, special low electrical impedance electrodes that could generate stable SEI at higher C-rates (1C) were used to test the additives' scalability under faster charging conditions. Under more challenging conditions, the NaPF₆ additive allowed for maintained capacity without showing any symptoms of lithium plating, even at 1C SEI formation rates.

To sum up, this work showed that NaPF₆ and KPF₆ are scalable and promising electrolyte additives for improving lithium-ion batteries' SEI properties under higher current densities. They are promising for next-generation battery systems, especially those aimed at fast-charging and long-cycle-life applications, because they provide an easy and affordable way to lower first-cycle losses and improve cycling stability. These results add to the larger body of knowledge in SEI engineering and offer important new information about how mixed-cation electrolytes can enhance the interfacial chemistry of lithium-ion battery systems.

Although the study's results are encouraging, more investigation is required to improve the electrode and electrolyte components in order to permit stable SEI production under high C-rate (fast-charging) circumstances. Although being the current standard, SEI layers generated at low C-rates with their higher impedance are here demonstrated to be less performing than electrolyte formed at higher rate for fast-charging conditions.

Future efforts should focus on:

- Continuing investigating inorganic electrolyte additives in conjunction with graphite-based electrodes with lower impedance that can enable SEI generation at high current densities because maintaining excellent surface stability and electrical conductivity.

- Expanding the selection of innovative inorganic additives beyond NaPF_6 and KPF_6 for electrolyte systems and electrolyte formulations that generate protective, ion-conductive SEI layers while maintaining chemical and electrochemical stability at high charging rates ($\geq 1\text{C}$).
- Utilizing operando methods to directly track SEI evolution during high-rate cycling, such as in-situ XPS or in-situ EIS.

For the next generation of lithium-ion batteries intended for grid-scale applications and electric vehicles, where quick charging and extended cycle life are crucial, stable SEI production at industrially relevant C-rates will be necessary.

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