

Electrochemical Degradation Mechanisms in Lithium-Ion Batteries: Understanding Capacity Fade and Pathways to Extended Cycle Life

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Lithium-ion batteries power modern electric vehicles, but their performance degrades over time due to chemical processes occurring inside the battery. This paper examines the main degradation mechanism: solid electrolyte interphase (SEI) formation at the battery's negative electrode. The SEI layer traps lithium and increases resistance, reducing both the battery's capacity and power. Three solutions show promise: silicon anodes (which store 10 times more lithium than graphite but expand significantly during charging), solid-state electrolytes (which are safer and enable better performance), and electrolyte additives like fluoroethylene carbonate (FEC) that create more stable protective layers. While each approach has challenges, recent research demonstrates practical progress: silicon composites achieving 90% capacity after 1,000 cycles and solid-state batteries operating across wide temperature ranges. Understanding these degradation processes is essential for developing the next generation of electric vehicle batteries.

I. Introduction

Lithium-ion batteries have revolutionized portable electronics and are now essential for electric vehicles. Sony commercialized the first rechargeable lithium-ion battery in 1991 using a graphite anode and lithium cobalt oxide cathode [3]. Today, these batteries power millions of electric vehicles worldwide.

However, battery performance inevitably declines over time. One of the most important degradation processes is the formation of a layer called the solid electrolyte interphase (SEI) at the negative electrode [1]. This layer consumes lithium and increases the battery's internal resistance, causing both capacity loss (the battery holds less charge) and power loss (the battery cannot deliver energy as quickly).

Understanding battery degradation is crucial for predicting how long batteries will last and for designing better batteries [2]. The goal of this paper is to explain how SEI formation limits battery life in electric vehicles and to review three promising solutions: silicon anodes, solid-state electrolytes, and electrolyte additives.

II. How Lithium-Ion Batteries Work

A. Basic Components

A lithium-ion battery has three main parts [4]:

- **Positive electrode (cathode):** Usually made of lithium cobalt oxide (LiCoO_2) or similar materials
- **Negative electrode (anode):** Usually made of graphite
- **Electrolyte:** A liquid that allows lithium ions to move between the electrodes

A porous separator keeps the electrodes apart while allowing ions to pass through.

B. Charging and Discharging

During discharge (when the battery powers a device), lithium atoms at the graphite anode lose electrons and become lithium ions. The reaction is:



The lithium ions travel through the electrolyte to the cathode, while electrons flow through the external circuit providing electrical current. At the cathode, lithium ions combine with electrons:



During charging, this process reverses—lithium ions move back to the graphite anode. This back-and-forth movement is why lithium-ion batteries are sometimes called "rocking chair" batteries [1].

C. Intercalation

In graphite, lithium ions insert between layers of carbon atoms in a process called intercalation [5]. Graphite in its fully charged state (LiC_6) can store 372 mAh of charge per gram of material [3]. This intercalation must happen without breaking the graphite structure for the battery to work reliably over many cycles.

III. The SEI Problem: Why Batteries Degrade

A. What is the SEI?

The solid electrolyte interphase is a thin layer that forms on the graphite anode surface when the liquid electrolyte touches the electrode [1]. This happens because the graphite operates at a voltage where the electrolyte is not stable - it breaks down chemically.

During the first charge, about 10% of the battery's capacity is lost to form this initial SEI layer [1]. The SEI contains various compounds including lithium fluoride (LiF), lithium carbonate (Li_2CO_3), and lithium oxide (Li_2O) [1]. At high

temperatures, compounds like LiF and Li_2CO_3 dominate, which increase the battery's internal resistance [7].

B. Why the SEI Causes Problems

While the SEI initially protects the electrode from further reaction with the electrolyte, it continues to grow slowly over time [6]. This causes three main problems:

- 1) **Lithium consumption:** Lithium ions get trapped in the growing SEI layer and cannot participate in charging and discharging, reducing capacity [1]
- 2) **Increased resistance:** The SEI blocks the flow of lithium ions and clogs pores in the electrode, increasing resistance and reducing power [1]
- 3) **Electrolyte loss:** The chemical reactions that grow the SEI consume the liquid electrolyte [1]

Research shows that SEI growth dominates battery aging in the early stages, with resistance steadily increasing until the battery loses about 10% of its capacity [8]. The growth rate slows over time but never completely stops.

C. How SEI Interacts with Other Degradation

Battery degradation is complex because different mechanisms interact. For example [1]:

- Cracking of electrode particles exposes fresh surfaces where more SEI forms
- Metal ions from the positive electrode dissolve and deposit on the negative electrode, accelerating SEI growth
- When lithium plates on the electrode surface (forming metallic lithium), it reacts with the electrolyte to form even more SEI

These interactions create feedback loops that can cause battery degradation to accelerate suddenly after initially stable performance.

IV. Solution 1: Silicon Anodes

A. Why Silicon?

Silicon can store far more lithium than graphite - its theoretical capacity is about 4,200 mAh/g compared to graphite's 372 mAh/g [9]. This means a silicon anode battery could potentially hold more than 10 times as much charge in the same space, enabling electric vehicles with much longer driving ranges.

B. The Volume Expansion Problem

The major challenge with silicon is that it expands dramatically when it absorbs lithium ions. The volume increases by about 320%, creating enormous mechanical stress [9]. This stress causes the silicon to crack and crumble, and particles can detach from the current collector. Early silicon batteries lost most of their capacity in just 10 cycles [9].

C. Solutions: Making Silicon Work

Researchers have developed several approaches to solve the expansion problem:

Nanostructuring: Making silicon particles extremely small (less than 150 nm) helps them withstand the expansion stress without breaking [10]. Nanoparticles have shorter distances for lithium to diffuse and can better accommodate volume changes.

Silicon-carbon composites: Mixing silicon with carbon materials creates a structure where carbon buffers the silicon expansion and maintains electrical connections [11]. The carbon coating also helps form a more stable SEI layer.

Porous structures: Creating materials with tiny pores gives the silicon room to expand into, preventing the structure from breaking apart [12]. One design using "ant-nest-like" porous silicon achieved 1,271 mAh/g capacity with 90% capacity remaining after 1,000 cycles [13].

D. Commercial Progress

Silicon anode technology is moving toward commercial use. In 2021, the company Enovix shipped the first silicon anode batteries to customers, and Sila Nanotechnologies began supplying silicon anode materials to device manufacturers [9]. BMW announced plans to use Sila's technology to increase battery capacity by 10-15% [9].

V. Solution 2: Solid-State Electrolytes

A. Replacing the Liquid

Instead of using a flammable liquid electrolyte, solid-state batteries use solid materials to conduct lithium ions between electrodes. This offers two major advantages: improved safety (solid electrolytes don't catch fire) and the ability to use lithium metal anodes with even higher capacity than graphite [14].

B. Sulfide Electrolytes

Among solid electrolytes, sulfides show the most promise because they conduct lithium ions very well—some achieve conductivities of 1.7×10^{-2} S/cm, which exceeds typical liquid electrolytes [15]. This high conductivity comes from sulfur's chemical properties: it is larger and less electronegative than oxygen, making it easier for lithium ions to move through the material [16].

Sulfide electrolytes are also mechanically flexible, which helps them maintain good contact with electrodes as the battery operates [16]. This is especially important for silicon anodes that expand and contract during use.

C. Performance Achievements

Recent research demonstrates impressive performance. A battery using a pure silicon anode with a sulfide solid electrolyte achieved [14]:

- High current capability (5 mA/cm²)
- Wide temperature range (-20°C to 80°C)
- 80% capacity retention after 500 cycles

Another study showed silicon anodes with elastic solid electrolytes achieving 90.8% capacity retention after 300 cycles without requiring external pressure [17], solving a major manufacturing challenge.

Solid-state batteries can achieve energy densities above 350 Wh/kg at the cell level, compared to below 300 Wh/kg for conventional lithium-ion batteries [14].

D. Remaining Challenges

Despite this progress, challenges remain. Sulfide electrolytes are sensitive to air and moisture, producing toxic hydrogen sulfide gas when exposed [15]. The interface between the solid electrolyte and electrodes can have high resistance, limiting performance. Manufacturing processes also need development for large-scale production.

VI. Solution 3: Electrolyte Additives

A. FEC: A Stabilizing Additive

Fluoroethylene carbonate (FEC) is a chemical additive that can be mixed into conventional liquid electrolytes to improve battery performance. FEC works by decomposing early during battery operation to form a better SEI layer [19].

When FEC breaks down, it creates lithium fluoride (LiF) nanoparticles that form a dense, uniform, and thin SEI layer [19]. The SEI formed with FEC contains both LiF (which conducts lithium ions) and elastic polymer materials (which can flex as the electrode expands and contracts) [18].

B. How FEC Improves Performance

FEC provides several benefits:

- Creates a more stable SEI that reduces ongoing electrolyte consumption
- The LiF in the SEI promotes uniform lithium-ion flow, suppressing dendrite formation [18]
- The flexible polymer components accommodate volume changes in silicon anodes [18]
- Improves both capacity retention and Coulombic efficiency (the percentage of charge that can be extracted) [20]

Research using advanced microscopy showed that FEC creates an SEI layer about 5 nanometers thick initially, growing to 7 nanometers during battery operation [21]. This controlled growth is much better than the uncontrolled growth seen without additives.

C. Optimal Use

Studies find that 10% FEC by volume in the electrolyte provides good performance improvement [18]. Too much FEC (above 50%) can cause problems by forming layers on the positive electrode that reduce capacity [23]. This shows that electrolyte optimization requires careful balancing of effects at both electrodes.

One limitation is that FEC's benefits take time to develop. Early cycles show similar degradation to batteries without FEC, but as cycling continues, FEC gradually redirects reactions to form more stable products [22]. This delayed effect means batteries need several cycles before the full benefits appear.

VII. Discussion and Future Directions

A. Comparing the Approaches

Each solution addresses battery degradation differently:

Silicon anodes offer the largest capacity improvement (10× increase) but face the most severe challenges from volume expansion. Current solutions using nanostructures and composites work well but add manufacturing complexity.

Solid-state electrolytes provide the most comprehensive solution—better safety, higher capacity, and stable interfaces. However, they require completely redesigning how batteries are manufactured and face challenges with air sensitivity and cost.

Electrolyte additives like FEC offer the easiest implementation since they only require changing the electrolyte formulation. They provide immediate improvements but cannot match the performance gains of silicon anodes or solid-state electrolytes.

B. Combining Approaches

The best future batteries will likely combine these strategies. For example, using silicon-carbon composite anodes with FEC additives can achieve much of the benefit of pure silicon while using existing manufacturing processes. Longer term, solid-state electrolytes will enable full use of silicon anodes by eliminating liquid electrolyte reactions.

Recent demonstrations show this synergy. Batteries using silicon with solid electrolytes have achieved 80% capacity retention after 500 cycles across temperatures from -20°C to 80°C [14]—performance impossible with any single approach alone.

C. Why This Matters

Understanding battery degradation helps in three ways:

- 1) **Better battery management:** Knowing how batteries degrade allows systems to optimize charging patterns to extend life
- 2) **Improved designs:** Understanding mechanisms guides development of better materials

3) **Cost reduction:** Longer-lasting batteries reduce the total cost of electric vehicle ownership

The complex interactions between degradation mechanisms—where SEI growth triggers particle cracking, which exposes more surface for SEI formation—show why understanding battery chemistry is essential for improving technology.

VIII. Conclusion

Solid electrolyte interphase formation is a critical challenge limiting the lifespan and performance of lithium-ion batteries in electric vehicles. The SEI layer traps lithium ions and increases resistance, causing both capacity and power to fade over time.

Three promising solutions address this challenge:

- **Silicon anodes** provide 10× higher capacity than graphite but require nanostructuring and composite designs to manage volume expansion. Recent results show 90% capacity retention after 1,000 cycles is achievable.
- **Solid-state electrolytes**, especially sulfides, offer high ionic conductivity ($> 10^{-3}$ S/cm), improved safety, and stable interfaces with silicon. These enable batteries with energy densities above 350 Wh/kg.
- **Electrolyte additives** like FEC create stable, LiF-rich SEI layers that suppress dendrite growth and accommodate electrode volume changes, offering immediate improvements with existing technology.

These approaches are moving from research laboratories toward commercial products. Companies are incorporating silicon-carbon composites into production batteries, and solid-state prototypes have demonstrated practical performance. The combination of these strategies provides a clear path to next-generation batteries with significantly improved capacity, safety, and lifetime.

Understanding the chemistry of battery degradation has revealed how complex the challenge truly is—different mechanisms interact, reinforce each other, and create feedback loops that cause sudden performance drops. This complexity demonstrates why rigorous scientific research is essential for developing better energy storage technologies. As batteries continue to improve through advances in materials chemistry, electric vehicles will become more practical and affordable, contributing to a more sustainable transportation future.

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