Chapter 1

Introduction

1.1 Background

The most promising solid electrolytes for electric applications are organic polymers, inorganic sulfides, oxides, and halides. Among them, sulfides are particularly favored and promising for electric vehicle (EV) applications due to their excellent lithium-ion conductivity and ductile nature, which allows them to be easily shaped and densified into various formats[2]. Additionally, wet coating of sulfide sheets with binders can be done using conventional electrode production methods. However, it is important to note that many sulfides have a limited electrochemical window. This means that when they are used with cathode active materials or metallic lithium, an additional protective layer is required to ensure their stable and safe operation.

The all-solid-state battery demonstrated by the research group from Samsung offers a practical and viable solution for sulfide-based solid-state batteries by incorporating a thin composite layer of carbon and silver. The separator was produced using a wet coating method, where a sulfide slurry was coated onto a non-woven fabric sheet together on a sacrificial substrate. This technique allows for the mass production of free-standing sulfide separators on a large scale. To enhance the cells interface properties, a warm isostatic presser (WIP) was employed to densify some of the components and cells. This process ensures strong interfacial contact between the different battery components and reduces interfacial resistance, leading to improved overall battery performance.

Excellent battery cycling performance was achieved in a pouch cell format (0.6 Ah) with coulombic efficiency of over 99.8% over 1000 cycles and incredible energy density of over 900 Wh/l[1]. This invention demonstrates the potential to scale up sulfide-based solid electrolytes, making them suitable for electric vehicle (EV) applications by meeting the energy density and safety requirements. The silver-carbon composite layer offers a viable solution for lithium metal batteries, introducing the concept of anode-free solid-state batteries.

Following the significant increase in energy density, there has been a surge of interest in the field of anode-free solid-state batteries, particularly in the study of the silver-carbon composite layer and other deposition-type anodes.

In 2021, the same research group published a paper showcasing the use of metal-carbon deposition layers with metals such as Zn, Al, Sn, Ni, and Ag[3]. Among these metals, silver (Ag) stands out as the most promising, exhibiting higher rate capability retention and discharge capacity retention over extended cycling periods. The research group highlights the crucial role of the carbon black layer, which electrochemically reduces lithium-ions, facilitating their accumulation and oversaturation[3].

Recent investigations have explored the structural changes in the silver-carbon composite layer of anode-free solid-state batteries[4]. Researchers have confirmed that lithium-ion intercalation first occurs within the carbon structure, followed by alloying with silver nanoparticles. When charging rates are higher, lithium tends to intercalate with carbon more readily, delaying the alloying process. This causes more lithium to be deposited on the current collector's side. Silver nanoparticles play a key role in promoting uniform lithium deposition and preventing the formation of lithium dendrites. The carbon layer also plays a crucial role in suppressing dendrite growth.

However, among the previous research on this silver-carbon composite anode, there is still some directions open for research. This PhD work focuses on the following three categories:

a. **Choice of Conductive Carbon**: Various types of conductive carbon, such as carbon nanotubes and graphite, have been investigated and found to significantly enhance electronic conductivity within different ranges. This improvement in conductivity has the potential to enhance lithium deposition and further boost the overall battery performance.
b. **Selection of Metals**: Research has primarily focused on single lithiophilic metals, neglecting exploration into metal alloys, particularly eutectic alloys, for use in deposition-type anodes. Among the metals studied, silver has demonstrated superior performance. However, the high cost of silver nanoparticles presents a challenge. Replacing silver nanoparticles with more cost-effective eutectic alloys could be beneficial for scaling up production.
c. **Composite anode reconstruction**: Research has shown that after the initial charging cycles, lithium alloy tends to migrate toward the current collector. In subsequent cycles, metal particles become trapped between the carbon black and the current collector due to weak adhesion at this interface. To address this problem, a dual-layered design is proposed. First, a primary layer of metal particles is deposited on the current collector, followed by a second layer of carbon black, which acts as an intermediate layer between the metal particles and the solid electrolyte. This restructuring also improves the

manufacturing process by resolving the challenge of evenly dispersing nanoparticles within the carbon black matrix.

1.2 Motivation

In this PhD dissertation, extensive research has been conducted to explore the feasibility of implementing the anode-free concept in all-solid-state batteries, building upon the silver-carbon composite layer proposed by the research team from Samsung[1]. Various chemistry combinations and structural designs have been investigated to assess their potential for practical application.

As shown in Figure 1, three different anode-free approaches were investigated and discussed:

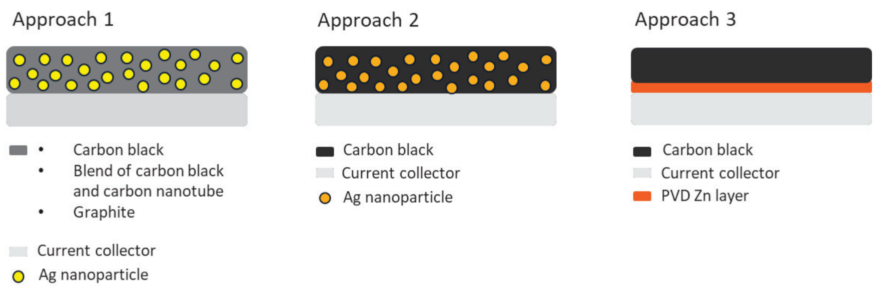

Figure 1. Cross-sectional view of various chemical compositions and structural configurations investigated in this PhD dissertation.

Approach 1: This approach begins with a baseline anode consisting of silver nanoparticles and carbon black. From this baseline, carbon black is either partially replaced with varying amounts of carbon nanotubes or entirely substituted with graphite. This allows for the investigation of different anode compositions, combining a lithiophilic metal (silver nanoparticles) with various conductive carbons.

Approach 2: In this approach, composite layers containing two different eutectic alloys were wet coated on the current collector. According to the literature[5], metallic elements such as Pb, In, Sn, Bi, Cd are capable of lithiation. The eutectic alloys composed of some of the aforementioned metals exhibit unique low melting temperature features. Since the incorporation of eutectic alloys into the system has not been explored in the literature, it is worth investigating.

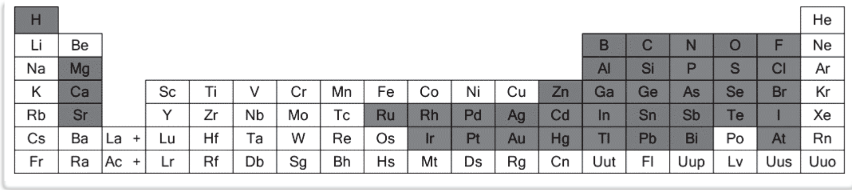

Figure 2. Summary of lithiophilic elements highlighted in grey from the periodic Table[5].

Approach 3: In this approach, a dual-layered anode was designed, consisting of a primary layer of physically vapor-deposited (PVD) zinc on the current collector and a secondary layer of carbon black positioned between the separator layer and the primary PVD-Zn layer. In comparison to silver, zinc is more abundant in the Earth's crust and tends to be more cost-efficient. Additionally, zinc has the advantage of being soluble in lithium during the lithium deposition process and exhibits zero overpotential, making it a competitive material as lithiophilic seeds in anode-free all-solid-state batteries[6].

This dissertation investigates key parameters crucial for the successful implementation of the anode-free concept in all-solid-state batteries. By discussing and analyzing these parameters, the research provides valuable insights and sets a research path for further advancements in this innovative battery technology.

Chapter 2

Theoretical Foundation

2.1 Overview of ASSB based on different electrolytes

Lithium-ion batteries have gained significant interest over the past few decades, particularly for their application in electric vehicles (EVs). However, the use of liquid electrolytes in commercial lithium-ion batteries raises safety concerns due to the flammable nature of organic solvents. Simultaneously, the increasing demand for higher energy density in terms of both gravimetric and volumetric energy densities from the EV market has prompted extensive international research and development efforts in exploring and advancing the next generation of batteries with different chemistries. This encompasses ongoing fundamental and applied research endeavors on a global scale[7].

Solid-state batteries have become increasingly popular in recent years due to their outstanding safety features and potential for high energy density. However, it is important to be cautious when claiming that solid-state batteries have higher energy density than commercial liquid-based batteries. For example, when comparing batteries with the same cathode and anode materials (e.g., graphite, silicon anode) and similar operating conditions, solid-state batteries tend to have a slightly lower energy density (266 Wh/kg) compared to conventional batteries with liquid electrolytes (277 Wh/kg)[8]. This is primarily because solid-state electrolytes are denser than liquid electrolytes, which affects the overall energy density of the battery. In the case of lithium metal, it possesses a high specific capacity of 3860 mAh/g and ultra-low negative potential of -3.040 V versus standard hydrogen electrode (SHE)[9]. What's more, lithium metal anode demonstrates better compatibility with certain solid electrolyte candidates[10]:

In a conventional lithium-ion battery with lithium metal anode, continuous side reactions can occur with freshly deposited elemental lithium due to the flowing nature of the electrolyte. Additionally, the growth of lithium dendrites through the solid electrolyte interface (SEI) can freely occur, potentially causing short-circuits in the battery. In terms of safety, the combination of a flammable liquid electrolyte and highly reactive lithium poses a significant risk, particularly in applications such as electric vehicles. On the other hand, in solid-state batteries, the porous separator soaked with liquid electrolyte is replaced by solid electrolyte, which offers an ionic pathway for ion transport while effectively insulating against electrons, thereby providing a