

Chapter 1

Introduction

1.1 Motivation

The increasing energy demand due to the growing prosperity in the industrialized countries and the economic rise of the developing and emerging countries on the one hand and the critical climate situation on the other hand requires a radical change of the current energy system. The use of renewable energies as a primary energy source can ensure a sustainable energy supply in the long term that is not based on fossil fuels. At this point in history, the decarbonization of the energy industry and the mobility sector is crucial. The increasing use of energy conversion technologies from renewable energy sources, such as photovoltaics or wind turbines, increases the share of electrical energy in the energy system. This, along with the energetically beneficial use of electrically powered motor vehicles, requires an ever-increasing need for electrical energy storage. Lithium ion batteries (LIB), as the leading energy storage technology, are currently the focus of research and industry and are widely used in portable electric appliances and vehicles. In general, compared with other battery systems, lithium (Li) batteries can provide high cell voltage and high energy density, require less maintenance and have longer life [1]. But improvements are still needed. Lithium deposition is a problem in Li batteries that limits their performance in terms of power and energy density. It must be emphasized that lithium deposition is a problem in both Li-ion batteries and Li-metal batteries (LMB), which is why the general term 'lithium batteries' is used. Two trends can be identified in the advancement of lithium batteries with respect to the problem of Li deposition: the optimization of the existing system (the state-of-the-art LIBs) and the further development of cell components such as active materials and electrolytes. This work

has tried to cover both topics.

Li-ion batteries: Lithium deposition in LIBs with intercalating electrodes can occur under harsh operating conditions such as high current density and low temperature or at a high state of charge[2]. Despite the tremendous research efforts on this topic, studies on the underlying causes are still needed to understand the root reasons for this phenomenon. This is the first step in optimizing the existing Li-ion batteries. On the atomic level, the influence of the mentioned conditions on the kinetics of cell components and more importantly on the properties balancing of cathode and anode can be noticed. In this study, with the help of the pseudo-two-dimensional modelling approach which is extended with two side reactions of anode, the transport mechanisms in a Li-ion cell are investigated. The kinetic imbalance between the anode and cathode induced by the aging effect is studied with the idea of calculating the ionic conductivity for different parts of the cell involved in the Li transport process. The change in ionic conductivity over a cycle and also the lifetime of the cell and its relation to the formation of unwanted lithium deposition are investigated.

Li-metal batteries: Lithium deposition in LMBs becomes undesirable depending on the growth structure. Because of the tendency for dendritic lithium deposition, LMBs generally exhibit low Coulombic efficiency, poor cycling performance, and risk of short circuit and subsequent thermal runaway, which limits their application. However, since the Li-metal anode has the highest specific capacity for lithium batteries, its realization is still of interest. This study expands its fundamental investigation of Li deposition by evaluating the LMBs under different operating conditions and liquid electrolyte compositions. Following previous LIB studies, the impact of the influencing conditions on the kinetics of the Li-metal anode and consequently on the growth of Li deposition is investigated.

Among the cell component developments studied, the transfer of LMBs to solid-state lithium batteries is highly desirable. Solid polymer electrolytes (SPEs) and especially polyethylene oxide (PEO)-based SPEs have attracted attention due to their desirable properties such as good solubility of Li-salts, processability and low cost [3–5]. In this study, the applicability of a PEO-based SPE in LMBs is investigated. With the aim of increasing the energy density, the compatibility of these SPEs with high voltage cathodes is investigated and methods to overcome the interfacial instability of cathode/SPE are introduced and studied.

1.2 Structure of this work

Chapter 2 first defines an electrochemical cell and presents the principles and governing equations. Then Li-ion batteries are introduced along with kinetics. The growth of Li-dendrites is also described. Later, the background of Li-metal batteries is explained and deposition mechanisms and growth conditions are discussed. Later, solid polymer electrolytes and essential parameters that will later be used in this work are explained. Finally, the instrumentation and experimental methods used in this work are clarified.

Chapter 3 is divided into two parts: The first part explains the transport regions in a Li-ion cell considered in this thesis. Then, the developed model to study the transport mechanisms of charge species in these regions is described. The governing equations and initial conditions are mentioned. In the second part, the experiments and methods related to the study of Li-metal cells with liquid electrolytes are explained. The cell structures, the performed experiments and the investigated conditions are described.

Chapter 4 describes the preparation of the solid polymer electrolyte and the NMC composite cathode fabricated in this work. Also, the passivating interlayers used to stabilize the NMC/PEO interface are introduced and the fabrication methods are explained. Later, the cell preparation and experimental methods are discussed.

Chapter 5 also consists of two main parts. The first part contains the results of the model used, which was explained in the first part of Chapter 3. The validation method is explained and the results of the calculations of the ionic conductivity in each of the transport regions are discussed along with the correlation of these values with the Li deposition reaction. The second part of this chapter provides the experimental results related to the performed experiments on the Li-metal cells, which are explained in the second part of Chapter 3. The experiments study the influence of the electrolyte composition, such as different Li-salts and their concentration, and the operating conditions, such as different temperatures and current densities. The results of galvanostatic cycling and electrochemical impedance spectroscopy (EIS) measurements are discussed.

Chapter 6 provides the experimental results on the SPEs and NMC composite cathodes prepared in Chapter 4. First, the ionic conductivity and electrochemical stability of the SPEs at different salt concentrations and temperatures are measured and discussed using EIS and cyclic voltammetry measurements. The compatibility of SPEs with NMC cathodes is discussed. The performance of various polymeric and non-polymeric interlayers is investigated and the results are discussed.

Chapter 2

Theoretical and experimental background

In this chapter, after a brief historical overview of electrochemical cells, the fundamentals and equations are discussed. Lithium-ion batteries are then introduced and the principle and kinetics are discussed. A separate section describes lithium metal batteries and their historical as well as modern challenges, which are related to lithium deposition and growth mechanisms. Solid polymer electrolytes are then presented as a possible solution for combination with a Li-metal anode. The ionic conductivity, mechanical properties and electrochemical stability of these electrolytes are presented as critical influencing parameters. Finally, the instrumentation and experimental methods used in this study are presented.

2.1 Electrochemical cells

The investigations of Luigi Galvani, an Italian physicist in 1790, led to the discovery of electrochemical reactions. Galvani noticed that contact between the scalpel and the crural nerves of the frog contracted all the muscles of its leg. He assumed the electricity was generated by the frog's tissue [6]. Alessandro Volta continued Galvani's observation and concluded that the current observed in the frog's body was due to two dissimilar metals in contact with the cellular fluid of the frog's tissue. Later, in 1800, he announced the first electric battery, the voltaic pile, in which he piled two types of metal disks (copper and zinc) separated by a felt embedded in sulfuric acid [7].

Electrochemistry is the understanding of the relationship between the flow of electrons and chemical reactions. Chemical reactions in which electrons are transferred are called redox reactions (reaction 2.1), involving two or more opposite half-reactions to ensure charge neutrality. A reduction reaction occurs when the species A accepts an electron and is reduced (reduction reaction 2.2). Oxidation, as the reverse reaction, takes place when species B donates an electron and is oxidized (oxidation reaction 2.3) [8]:



An electrochemical cell consists of 2 electrodes and an electrolyte in between which can be liquid, solid or gelified. In the case of liquid electrolyte, the two electrodes where the half-reactions occur are immersed in an electrolytic solution that offers ionic conduction and electroneutrality and the electrodes are separated by an electrolyte-permeable separator. Due to charge conservation, in these cells, the energy of a redox reaction in the form of electricity can be obtained so that electrons, e^- , flow over an external circuit and perform electrical work. The electrode with the higher potential is called the positive electrode, and the one with the lower potential is called the negative electrode. The maximum potential difference measured between the two electrodes under equilibrium condition is called the electromotive force (EMF), which is directly related to the system's change in the Gibbs free energy, as shown in Equation (2.4): [9]

$$\Delta G = -nFE, \quad (2.4)$$

where n is the mole of transferred electrons in reaction, F is the Faraday constant (96485.3 C·mol⁻¹), and E is the EMF. The change in Gibbs free energy of a redox reaction can be shown as in Equation (2.5):

$$\Delta G = \Delta G^\circ + RT \ln \frac{[R]}{[O]}, \quad (2.5)$$

where ΔG° is the change in Gibbs free energy under standard conditions (1 atm and 298 K), R is the universal gas constant (8.3145 J·mol⁻¹K⁻¹) and T is the temperature in K. $[R]$ and $[O]$ are the concentration of reduced and oxidized species. The cell potential under standard conditions (E°) (1 molar and 1 atm at 298 K) can be represented as in Equation (2.6):

$$\Delta G^\circ = -nFE^\circ \quad (2.6)$$

The use of Equations (2.4), (2.5) and (2.6) leads to the Nernst equation given in Equation (2.7):

$$E = E^\circ + \frac{RT}{nF} \ln \frac{[O]}{[R]} \quad (2.7)$$

The Nernst equation characterizes the potential for each of the electrodes. Thus, the cell voltage is the difference in potential between the two electrodes of a cell:

$$E_{\text{cell}} = E_{\text{Red}} - E_{\text{Ox}} \quad (2.8)$$

In electrochemistry, the electrode is called an anode where oxidation takes place and the other one is called a cathode where reduction occurs. In the field of rechargeable batteries, the redox reaction can be reversed during the charge and discharge process. In the work, the definition of anode and cathode are based on the discharge process. It means the positive electrode is defined as the cathode and the negative electrode as the anode.

In a battery, the cell potential decreases during discharge, the spontaneous reaction, due to the removal of energy from the system and the system approaches equilibrium conditions. During charge, the system moves out of equilibrium, the non-spontaneous reaction, due to the addition of energy, thus the cell potential increases. The energy stored in a galvanic cell (battery) is the outcome of the cell voltage (U) and the amount of charge (Q) that can be stored. The cell potential in the fully charged and fully discharged states is different. Therefore the energy stored in a cell can be calculated using the following:

$$W = \int_0^t IU(t)dt = Q \cdot U_{\text{avg}} \quad (2.9)$$

where W is energy (Wh), I is the current (A), U is the voltage (V), and Q is the magnitude of the charge storage capability of any material, known as capacity (Ah) [10]. The capacity is usually defined in Ah (1 Ah=3600 C) and can be normalized by weight, volume, or mole. The theoretical specific (normalized) capacity for a material can be computed using Faraday's law:

$$Q_{\text{th}}\left(\frac{mAh}{g}\right) = \frac{nF}{3.6M_w} \quad (2.10)$$

Where M_w is the molecular weight and n is the number of electrons exchanged per mole of active material. Similar to capacity, energy and power can be normalized by weight (gravimetric, Wh·kg⁻¹ or W·kg⁻¹) or by volume (volumetric, Wh·L⁻¹ or W·L⁻¹). Therefore, electrode materials with a high specific capacity, high voltage,

or both are needed to achieve the highest energy storage capability. In the periodic table, lithium is the lightest metal and has a high specific capacity of $3860 \text{ mAh}\cdot\text{g}^{-1}$ and a low electrode potential of -3.04 V vs. standard hydrogen electrode [11]. These characteristics make lithium-based systems the battery technology with the highest energy density, coupled with a long cycle life among the systems introduced to date. Cycle life is the number of cycles the battery can be reversibly charged and discharged as long as the performance is sufficient. The term ‘sufficient’ can be defined in various ways, e.g., as long as the capacity is greater than 80 % or 70 % of the initial capacity, or as long as energy is stored [12, 13].

A comparison between different battery chemistries in terms of energy and power density is shown in the Figure 2.1 known as the Ragone diagram [14].

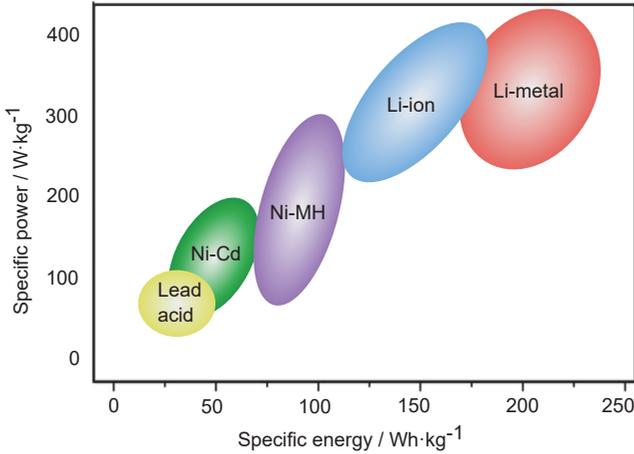


Figure 2.1: Traditional ragone plot of various rechargeable batteries showing the superiority of the Li-based battery systems.[14]

2.2 Lithium ion battery

Lithium-ion batteries (LIB) have proven to be an efficient energy storage system in terms of both energy and power density, reliability and cyclability.[15] Today, the state-of-the-art LIBs which are based on intercalating electrodes offer gravimetric energy densities up to $260 \text{ Wh}\cdot\text{kg}^{-1}$. [16]

Lithium ion batteries were first developed in the 1970s [17–19]. After two decades of intensive materials development, Li-ion cells were commercialized by Sony in 1991 [20, 21], which is shown schematically in Figure 2.2.

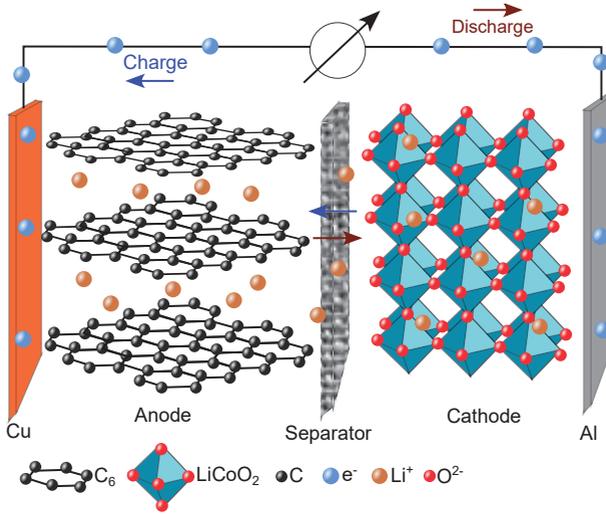
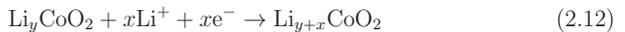


Figure 2.2: Schematic structure of a lithium-ion cell consisting of the graphite anode, coated on a copper current collector, and the LiCoO_2 cathode, coated on an aluminum current collector. A separator separates the two electrodes. Based on [22].

The active materials on the cathode side are usually deposited on aluminum foil which serves as a current collector. On the anode side, copper serves as the current conductor. The redox reaction taking place in these Li-ion cells during the discharge process is as follows:



During charging, the reactions reverse. During discharge, the intercalation of charge carriers, in this case Li-ions, into the lattice of the cathode active material takes place. The intercalation mechanism here is the insertion of a guest species (Li-ions) so that a new material is formed. Depending on the host lattice, the intercalation mechanism can be one-, two- or three-dimensional. LiCoO_2 as cathode material allows two-dimensional mobility of the lithium cation. Alternatives are, for example, olivine lattices as in LiFePO_4 , which allow one-dimensional linear mobility, or spinel lattices such as LiMn_2O_4 , which allow three-dimensional mobility in the spatial directions.[23]

During the charging process, the lithium ions are extracted from the cathode and intercalated into the anode active material, which is usually graphite. Graphite has been the most successful insertion anode material for commercial use to date due to its dimensional stability, higher specific charge, and lower potential (0.1 V vs Li/Li^+). The graphite anode has a layered lattice structure with a stacked arrangement of hexagonally cross-linked carbon rings (graphene). During charging, the Li-ions distribute between the graphene layers and form three stages of intercalation. The dissolved Li-salt in the electrolyte provides the lithium ions. Lithium hexafluorophosphate (LiPF_6) is widely used in commerce as a lithium conducting salt. The usual organic solvents for LiPF_6 are ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC), or ethyl methyl carbonate (EMC). Normally at low potentials decomposition of the commercial electrolyte solvent takes place. The decomposition compounds form an insulating but ion-conducting layer called solid electrolyte interface (SEI), which prevents the co-intercalation of the solvent together with the Li-ions into the graphite layers. The electrochemical stability window of the electrolyte controls the formation of passivation layers at the anode and cathode sides.

As illustrated in Figure 2.3 The gap between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of the electrolyte defines the electrochemical stability window (ESW). If the electrochemical potential of the anode μ_A is above the LUMO, the electrolyte will be reduced forming a passivation layer, SEI, until there is an electron barrier at the anode/electrolyte interface. If the electrochemical potential of the cathode μ_C is below the HOMO, a passivation layer is also formed with oxidation of the electrolyte until electron transfer is blocked. The cathode-side passivation layer is called the Conducting Electrolyte Interface, CEI.

The anode and cathode potentials, Φ_A and Φ_C are defined based on electrochemical
