Metal anodes for next generation secondary batteries. The case of Zn and Li

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To my grandmother Olga,
my role model of effort,
dignity and perseverance.
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Zinc is one of the most important materials in the battery industry. Since centuries, zinc has been widely used in the field of primary batteries due to its high energy density, relatively low price, great abundance on Earth, low toxicity and relatively easy manufacture process. Zinc showed its utility already in the 1800, when Volta proposed the conversion of chemical energy into electrical energy with a Zn/Cu cell. This idea was further developed by Daniell. Nevertheless, it was not until 1865 when Leclanché presented a newfangled non-rechargeable battery. The concept was based on the use of metallic zinc and manganese dioxide as the negative and positive electrodes, respectively, immersed in a solution of ammonium chloride. Years later, Jungner came up with the idea of using alkaline electrolytes instead of acidic. [1, 2] The Zn/MnO$_2$ alkaline cell was improved in the middle of the 20$^{\text{th}}$ century by Lewis Urry, who proposed the primary gel zinc anode. The main challenge was to increase the power, which was addressed by changing the negative electrode to powder zinc combined with an alkaline electrolyte gel. This has been one of the greatest contributions of the battery industry to the contemporary world. This battery has leaded the market for decades, positioning itself as one of the most widely used primary cells. [3]

![Figure 1](image_url)  
**Fig. 1** Adaptation from [2] with permission from The Royal Society of Chemistry. Theoretical energy density of various rechargeable battery systems vs. their practical energies compared with gasoline.

Figure 1 shows the practical and the theoretical energy density of different systems. The latter is presented in two ways: first considering only the active materials of the
electrodes, and secondly taking into account the other battery components, such as the electrolyte and the non-reactive additives (practical battery).

Despite the great advantages of zinc over other materials, its use has been limited to primary batteries. There are some limitations that need to be overcome for its successful use in rechargeable systems: dissolution of zinc oxide into zincates in alkaline media, evolution of hydrogen and mainly dendrite formation. In the decade of the 90’s, several attempts were focused into improving the life of the rechargeable zinc electrode. However, the emergence of other technologies diverted the attention. More recently, there has been a great effort to develop alternative energy sources in order to replace fossil fuels. Therefore, research has been focused once again on rechargeable systems with high energy density. Metal-air batteries are the most promising candidates. [4] The practical specific energy of these systems is tremendously high compared to other traditional secondary batteries which are commonly used at the moment. Zinc-air is of great interest because the cells can be manufactured with a competitive price in the market. [5]

Fig. 2 Theoretical and practical energy density of various types of rechargeable battery. Adapted from [4] with permission from John Wiley and Sons.

Concerning lithium based batteries, the interest in research and development of systems beyond Li-ion has increased during the last years. Among all anode materials, metallic lithium has a tremendous theoretical specific capacity (3860 mA h g⁻¹) and the lowest negative electrochemical potential (-3.040 V vs. SHE). Consequently, a new generation of batteries based on metallic lithium such as Li-air, Li-S and Li-Se are of great interest among other secondary cells due to their high theoretical energy density.
Figure 2 shows that the next generation of high energy density batteries relies on the use of metal anodes such as lithium and zinc. High energy density batteries are expected to play an important role in portable electronics and electric vehicle in which the weight of the battery is of key importance.
2 State of the Art

2.1 Chemistry of rechargeable alkaline zinc electrodes

One of the main advantages of the rechargeable zinc electrode over other technologies is its electrochemical reversibility in aqueous alkaline electrolytes. The fact of excluding organic solutions from rechargeable systems reduces significantly the manufacture costs. In addition, alkaline aqueous electrolytes have a high ionic conductivity at low temperature, and other electrodes with known long cycle life can be used at the positive side, e.g. Ni(OH)$_2$/NiOOH or MnO$_2$/Mn$_2$O$_3$.

Nevertheless, the charging process in a Zn electrode (reduction of ZnO to metallic Zn) remains as one of the challenge, since ZnO does not have a good conductivity and acts as an insulator. Moreover, there are three main drawbacks which need to be solved so that the zinc electrode can be efficiently used in rechargeable batteries: the dissolution into zincates, the hydrogen evolution reaction and dendrite growth. [6–8]

2.1.1 Dissolution into zincates

The dissolution of ZnO into solution proceeds via formation of tetrahedral complex ions, called zincates Zn(OH)$_4^{2-}$. Some authors suggest the presence of other species such as Zn$_2$(OH)$_8^{4+}$ (two nuclei). However, the zincate is the structure that prevails in the solution.

![Graph showing the solubility of ZnO in KOH](image)

**Fig. 3** Adaptation of the diagram of the solubility of ZnO in KOH. [9]

The solubility of ZnO is strongly dependent on the concentration of OH$^-$ (see figure 3). The influence of temperature is almost negligible. The solubility of ZnO results in a decreased cycle life of the electrode. After dissolution, zincates may move far from the vicinity of the negative electrode. During the charging process, the reduction may be affected by the lack of zincates at the electrode surface, which leads to shape change and dendrite formation. [5, 6]
The Zn/ZnO reaction taking place at the negative electrode involves the reduction of Zn\(^{2+}\) to metallic Zn during the charging process of a battery following these reactions [10]:

\[
ZnO + H_2O + 2OH^- \rightleftharpoons Zn(OH)_4^{2-} (aq) \tag{1}
\]

\[
Zn(OH)_4^{2-} (aq) + 2e^- \rightleftharpoons Zn + 4OH^- \quad E= -1.24 \text{ V vs. NHE, at pH 13} \tag{2}
\]

In practice, the reversible reaction of ZnO/Zn may be more complex than the two-step process described in reactions (1) and (2). Kinetic studies of Bockris [11] suggested that the reaction path most probably consisted in a four-step mechanism:

1. \[Zn(OH)_4^{2-} (aq) \rightleftharpoons Zn(OH)_3^{2-} (aq) + OH^-\] (Bulk of the electrolyte) \tag{2(a)}
2. \[Zn(OH)_3^{2-} (aq) + e^- \rightleftharpoons Zn(OH)_2^{2-} (ad) + OH^-\] (Rate determining step) \tag{2(b)}
3. \[Zn(OH)_2^{2-} (ad) \rightleftharpoons Zn(OH)_{(ad)} + OH^-\] \tag{2(c)}
4. \[Zn(OH)_{(ad)} + e^- \rightleftharpoons Zn_{(s)} + OH^-\] \tag{2(d)}

The zincate ion dissociates following four consecutive steps with two of them involving a single electron transfer. Since the step 2(a) is the only one that does not occur at the electrode surface, the local concentration of OH\(^-\) increases while the concentration of Zn(OH)\(_4\)\(^{2-}\) decreases near the electrode surface. This phenomenon contributes favorably to the dissolution of zinc oxide. Other mechanisms have been proposed. However, the majority of the studies in the field show consistent results which support Bockris’ mechanism.

The stability of species involved in the electrochemical reduction of zinc is represented in the Pourbaix diagram (see figure 4). The transversal dash lines represent the stability window of water. It can be noticed that zincate ions are not formed below pH 13.

The issue of ZnO solubility has been mitigated by several approaches such as the incorporation of Ca(OH)\(_2\) to the electrode, or phosphates, borate, carbonate and fluoride to the electrolyte. [12, 13] Nevertheless, the most successful approach has been to saturate the electrolyte with zincates ions. Thus, alkaline zinc batteries are belonging to the cases where the active material is not only located in the electrode itself. [14]
As a consequence of the oxidation processes of metallic zinc and the dendrite formation, an undesired secondary effect takes place at the electrode: the shape change of the material. The dissolution of ZnO into zincates leads to a rearrangement of particles and areas of the current collector can even become bare. [16, 17] In order to inhibit the shape change in the electrode, the use of additives in the electrolyte has been proposed, which can reduce the solubility of zincates (e.g. KF and K$_2$CO$_3$).[18, 19] Other attempts have focused on the modification of the structure of the current collector or on the architecture of the zinc electrode to ensure a uniform current density.[20]

Another side effect of the dissolution of metallic zinc is the passivation of the electrode. This process is also called corrosion and occurs due to the formation of a barrier layer near the zinc active sites.[21] The concentration of zincates exceeds the maximum solubility and leading to precipitations in the form of compact zinc oxide. This phenomenon causes losses in the capacity of the electrode. [22, 23]. Some organic additives such as polyethylene glycol (PEG) are the most promising additives to inhibit passivation of zinc, since these molecules adsorb at the zinc surface. [24–28]

### 2.1.2 Hydrogen evolution during the electrodeposition of Zn

The Pourbaix diagram (see figure 4) clearly shows that the hydrogen evolution reaction (HER) is thermodynamically favored over the deposition of metallic Zn. At pH values higher than 13, the standard potential of Zn electroplating is -1.24 V vs. NHE.

---

**Fig. 4** Adaptation of Pourbaix diagram for the system Zn-water at 25°C. [15]
This potential is outside the stability window of water, represented in the diagram as the cross-lines (a) and (b). Under this high alkaline condition, hydrogen evolution is proceeding via reaction (3):

\[
2H_2O + 2e^- \rightarrow H_2(g) + 2OH^- \quad E = -0.828 \text{ V vs. NHE}, \text{ at pH 13} \quad (3)
\]

HER is, in this case, an undesired side reaction which decreases the cycle life of a zinc electrode. It deteriorates the electrode surface and also increases the internal pressure. Additionally, this side reaction causes convection forces in the electrolyte, thus the deposition of zinc on the current collector is affected by the transport of the material due to the presence of bubbles.[7] Rogers et al. used a rotating disk electrode to study the electrodeposition of zinc in alkaline electrolyte and to separate the influence of HER. [8] The results were highly valuable because it was found that dendrite formation of zinc actually favors the HER strongly depending on the concentration of the electrolyte, the paste electrode composition and the current density. Several solutions have been proposed to overcome this issue. They can be grouped into two areas: adding additives to the electrode or to the electrolyte.

Metals with a high overpotential for HER, such as Pb, Hg, or Cd can be used to address this issue.[30] A metal oxide can be added to the paste electrode. During the charging process (cathodic process), the metal is reduced forming a conductive network which is retarding HER at the electrode. However, the use of these heavy metals is highly regulated due to the impact of the residues to the environment. Therefore, other metals such as Ni, In and Bi were also proposed since they can provide a similar effect. [31–33] On the other hand, additives to the electrolyte have been also studied. More concretely, organic acids show benefits to hinder HER, especially tartaric, succinic, citric or phosphoric acid. The overpotential for HER increases, since an adsorption process of acid molecules takes place on top of the zinc surface, which blocks the active sites for HER. [34]
2.2 The dendrite formation at the Zn metal anode in alkaline electrolyte

Besides dissolution of ZnO into zincates and HER, there is a third challenge which is the preferential growth of the metal in a dendritic shape during the electrodeposition. Actually, the dendritic growth is the main issue since it natively affects the other two issues. Dendrites grow following the current lines towards the positive electrode resulting in the perforation of separators. When this occurs, the positive and negative electrodes are in direct electric contact, which causes the short circuit of the battery. Actually, the dendritic growth is the main issue since it does not only lead to short-circuit but also affects negatively the other two issues such as passivation or HER.

The electrochemical deposition of metallic zinc during charging of a battery is a process far away from equilibrium. Depending on the overpotential applied, different morphologies can be obtained. More homogeneous films are obtained at low overpotentials.[35] However, the rate of growth is too low and higher overpotential is required for more realistic applications. These demanding conditions move the system even further away from equilibrium. The mass transport and surface kinetics are the most important factors to determine the crystal shape.

![Schematic representation of the diffusion limited process during metallic zinc deposition in alkaline media.](image)

**Fig. 5** Schematic representation of the diffusion limited process during metallic zinc deposition in alkaline media. (a) Dendrite growth. (b) Branching growth. Figure 5(b) was adapted with permission from [36]. Copyright 2006, American Chemical Society.

Figure 5a illustrates the process of deposition of zinc under alkaline conditions. Once cathodic current is applied to the electrode, the concentration of zincates is depleted near the electrode surface. Zincates are consumed triggering their diffusion from the bulk of the electrolyte to the interface. The growth rate in some areas is faster than in other areas due to the difference in the zincate diffusion to those areas. While planar diffusion occurs at flat areas, hemispherical diffusion with enhanced mass transport takes place at sharp areas such as dendrites.[37, 38] This difference in the depletion zones generated by the mass transport limitation is illustrated in Figure 5b. The growth is faster at sharp structures than at facets of the polyhedron due to the enhanced mass transport (higher concentration of zincates).

From the literature, it is known that dendrites are formed at overpotentials higher than 80 mV.[9] Authors have found that at a fixed overpotential, the dependence of total deposition current is quadratic with time \( I = kt^2 \). This correlation is due to an
increase in the surface area because of dendrite formation. [38] The high surface area is not beneficial since it increases also the corrosion of the zinc electrode via hydrogen evolution.

Fig. 6 Scheme of the nucleation and growth process of metal nuclei at different deposition rates. Adapted with permission from [39]. Copyright 2001, American Chemical Society.

The nucleation of particles is a key step to predict the final morphology of the resulting film. [40] Penner [39] suggested that the early stages of the formation of particles are governed either by kinetics or by diffusion, depending on the overpotential applied (see Figure 6). The rate of consumption of ions during electrodeposition is much higher when high overpotentials are applied and a broader depletion layer around the nucleus is formed. This causes interparticle diffusion coupling (IDC) because the layers of different nuclei overlap. Final results show that particles with overlapping diffusion layers grow slower than those which are isolated. On the other hand, IDC can be avoided when the system is subjected to kinetic control. Nevertheless, the use of low overpotentials to grow particles implies a substantial increment in the time of deposition as well as promote thermodynamically favored HER. Therefore, a balanced situation is desired, if a reasonable amount of time is used to grow a more homogeneous film, with a uniform distribution in the nuclei size.

2.2.1 Strategies to mitigate dendrite formation in alkaline electrolyte

a. Electrode additives

One of the strategies proposed to inhibit dendrite formation is to incorporate additives to the paste electrode. Three main categories are found in literature: heavy metal oxides, alkaline earth metal oxides or hydroxides, and polymeric additives.
The reduction of metal oxides to metallic compounds such as Bi, Tl, Ga, Hg, Pb, Cd and In, results in a significant improvement in the life cycle of the zinc alkaline batteries. Such improvement is mainly due to the high overpotential for HER of those metals.[30–34] Nevertheless, the metal also forms an internal network in the paste electrode. This network improves the electronic conductivity and the current distribution all over the electrode, making it more feasible to form a more compact thin zinc deposit. Researchers have found differences in the influence of these metals in the performance of the electrode. Mercury, for example, is not recommended since it increases the rate of shape change of zinc electrodes. In addition, its use is restricted due to its environmental impact. Indium and thallium are the most suitable alternatives. It has been reported that these metals have a positive influence on the shape change and on the current distribution, due to a change of the polarizability of the electrode. [30] Typically, the oxide additives have a proportion between 1 and 4% of the paste electrode.

In the second group of additives, Ca(OH)$_2$ and Bi$_2$O$_3$ are the most commonly used. The shape change is minimized with the use of calcium hydroxide due to the formation of calcium zincate [Ca(OH)$_2$Zn(OH)$_2$·2H$_2$O] which reduces the solubility of zincates that move away from the vicinity of the electrode. The effect of bismuth oxide is the creation of a conductive network, similarly to what the heavy metals provide.[13] More recently, a ceramic conductor (TiN) was proposed which retains zincates ions leading to a more uniform deposit, since titanium nitrate in contact with the alkaline electrolyte forms zincate conductive binding zones [41, 42]

The category of organic compounds focuses on exploring the mechanical properties of these materials. By their incorporation into the paste electrode, a stable network is built to retain the zincates ions near the current collector of the negative electrode. PTFE [43] and polyvinyl alcohol [44, 45] are the most commonly used binders.

b. Electrolyte additives

The use of additives has been also extended to the electrolyte. In addition to hydroxyl and zincates ions, some authors reported improvements in the reduction of dendrite formation and, consequently, in the cycle life when organic additives are present in the electrolyte. Some of these additives have the role of controlling the deposition rate by blocking sites due to the specific adsorption of the organic molecules at the surface. Generally, quaternary salts have been reported but also surfactants such as thiourea and poly(ethylene glycol). [46–49] A second type of organic additives used to retard the kinetics is carboxymethyl cellulose or starch-based derivatives. [50] However, it is necessary to consider that the internal cell resistance will most probably increase due to the decay of the ionic mobility.
c. Separators

In principle, the main role of the separators is to serve as a reservoir of electrolyte and to prevent the short circuit of the battery by acting as a barrier to separate physically the positive and negative electrodes. A separator must be electrically insulating, wettable and resistant to the chemical conditions of the cell. The ionic conductivity must be as high as possible. It should prevent the migration of particles through the cell. In addition, it is important to have mechanical stability and flexibility. For many years, cellophane was the separator of choice because it fulfills all these requirements. Nevertheless, in alkaline conditions cellophane is not stable.

Zn dendrite growth towards the negative electrode (penetrating the separator) can be avoided by using microporous separators. Different separators have been developed to be employed for the zinc electrodes, e.g. polypropylene, cross-linked polyalkenes, poly(vinyl alcohol), coated with metal, non-woven polymers and multilayers. Microporous polypropylene has been proven to be effective in resisting to dendrite penetration. Its main drawback is the ion selectivity.[51] Polyalkene membranes are excellent since they provide a tortuous pathway for the dendrite which hinders the penetration. Unfortunately, they also favor a shape change because the electrodes expand during cycling due to the fact that the separators do not swell.[52] Poly(vinyl alcohol) was another alternative since it is more favorable to swell. However, it is not mechanically stable. [53] Another strategy consists in incorporating additional polymer separators coated with metals. The idea is to oxidize the tip of the dendrites, once they touch the coating. The results showed that this does not prevent dendrite formation, it just retards the penetration.[54, 55] More recently, a combination of polymers in a non-woven texture has yielded excellent results. Fibrous polypropylene (PP), poly(vinyl alcohol) (PVA) and polyamide are superposed on top of each other, neither woven nor knitted arranged. The achieved porosity can be very high (75% pore volume), which favors the electrolyte retention. The disorder of the structure makes these separators resistant to dendrite penetration. The last type are the multilayer separators, where different pore size separators are compiled in order to prevent dendritic growth as well as retaining zincates ions near the vicinity of the negative electrode.[56, 57]

d. Modification of charging protocol

Zinc electrodes are recharged by applying a constant direct current (DC) density. It causes depletion in the concentration of zincates ions near the electrode surface, which promotes dendrite formation. Besides the introduction of additives to the cell, some decades ago efforts were devoted to prevent dendrite formation by applying non-conventional charging protocols. Different methods were studied: pulse current (PC), pulse-reverse current (PRC), alternating current superimposed on direct current (AC-DC), alternating voltage (AV) and alternating voltage superimposed on constant voltage (AV-CV).
Aroute et al. reported a study explaining the positive effect of pulsating charge current on the formation of zinc dendrites.\cite{58} He suggested that with this method, the zincate concentration gradient can be modified during the breaks, since there is enough time for the diffusion of the ions from the bulk to the interface to take place. Other attempts were focused in the application of alternating current (AC). They concluded that charging at higher frequency currents is not beneficial for Zn electrodes because there is not enough time to reestablish the concentration of zincates.\cite{59} However, positive results were obtained when frequencies were kept below 10 Hz.\cite{60} The application of an alternating voltage (AV) was explored by Chin’s group. They found that a smoother surface could be obtained if an AV is superimposed to low constant overpotentials, since it increases the rate of nucleation. The last contribution to the field proposed the application of a multicomponent charging current.\cite{61} Not only intermittent negative current was included in the protocol, but also reverse steps with anodic currents. Nevertheless, this last approach was discarded because the time required for the charging process was too long, namely, four times higher than that of a simple pulsed charging protocol.\cite{62, 63}

The large variety of parameters involved in the pulse charging protocols \cite{64} may have led to contradicting conclusions reported in literature and discouraged scientists in further exploring this approach.
2.3 Preferential growth at Li metal anodes in organic electrolytes

As in other metal anodes, the main drawback of using lithium metal as anode in rechargeable batteries is its dendritic growth upon cycling.[65, 66] The formation of this type of morphology causes short circuit of the battery. Also, it raises the probability to isolate active material, because the dendrites can break and disconnect from the anode core ("dead" lithium).[67] The high surface area of this type of morphology promotes side reaction, e.g. decomposition of electrolyte, thus increasing the consumption of electrolyte. All these aspects influence negatively the cycle life and columbic efficiency of the battery. Last but not least, safety issues arise with high surface area lithium (thermal runaway and explosion of batteries).[68]

The electrochemical mechanism of metal deposition has been widely studied in aqueous solution, e.g. silver, copper, zinc.[4, 36, 39, 69, 70] Nevertheless, the nucleation and growth of lithium which requires organic electrolytes has to consider additional factors such as the formation of the solid-electrolyte interphase (SEI) layer. Recently, simulation has confirmed that the preferential growth of lithium is influenced by a competition between the timescales of the cation diffusion and reductive cation deposition at the anode interface. These two factors would determine if the deposition is favored at the substrate or at the previously deposited dendrite tips.[71, 72]

\[ \text{Li}^+ + e^- \rightarrow \text{Li}_{(s)} \quad E^\circ = -3.04 \text{ V vs. NHE} \quad (4) \]

The preferential electrodeposition of metallic lithium is also governed by the applied current density, i.e. high current densities promote dendrite formation. The morphological changes of metallic lithium also influence the SEI layer. Roughening of the lithium electrode increases the surface area which requires building a new SEI layer (see figure 7).[73–75]

**Fig. 7** Schematic representation of lithium metal growth at low and high current densities. S.L.: SEI layer. Adapted with permission from [76]. Copyright 2000, American Chemical Society.
2.3.1 Strategies to mitigate dendrite formation in organic electrolyte

a. Organic solvents

Currently, the most commonly used solvents are: dimethoxyethane (DME), diethyl ether (DEE), propylene carbonate (PC), ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC).[77–80] In addition to the factors previously discussed, it is known that the organic electrolyte has also a strong influence on the morphology of the deposit.

Two combinations of organic solvent-salt are promising to mitigate the dendrite formation. First, PC/DMC electrolytes with low content of PC demonstrated to be beneficial to retard dendrite formation if LiTFSI [bis(trifluoromethane sulfonyl)] salt is present.[81] Secondly, 1,3-dioxolane (DOL) in combination with LiClO$_4$ or LiAsF$_6$ hinders lithium dendritic growth. It was proposed that the SEI layer formed with these compounds is more flexible due to formation of polydioxolane oligomers produced by the reduction of DOL. A flexible SEI could adjust to changes in morphology more easily. Therefore, lithium is protected and the battery may have a longer life.[82]

b. Lithium salts

In addition to organic solvents, lithium salts are part of the non-aqueous electrolyte used in Li-metal batteries. Therefore, salts can also have an effect on the properties of the SEI layer. It was reported that the salt concentration may influence in the lithium dendrite formation. The improvement in the cycle life of Li-S batteries is significant when the electrolyte has a concentration of 7 M Li salt, since the formation of polysulfides also is dependent on the concentration of Li$^+$. Nevertheless, the main disadvantage of this strategy is the high cost for real applications.[83, 84]

c. Formation of polymeric layers

Polymer electrolytes (PE) increase the mechanical strength of the SEI layer. Polyethylene oxide (PEO) was proposed to be employed in Li batteries already in the 70’s. It is chemically stable in contact with lithium, and shows promising cyclability. [85] Still, it only operates below 80 °C. Higher temperatures influence negatively its mechanical strength.[86] However, PEO is not efficient in blocking the penetration of dendrites regardless of the temperature. A mixture of PEO and polypropylene oxide (PPO) has been tested in combination with salts and EC/PC electrolyte. No successful results were found.[87] Nevertheless, block copolymers enhanced the mechanical stability of PEO because they form channels with Li$^+$ which generates a more rigid network. [88]

Among all polymers, gel polymer electrolytes (GPE) have shown the most successful results to prevent dendrite formation. Specifically, poly-acrylonitrile (PAN) is the
most efficient polymer in this task. Addition of 5-10 % of PAN to a PC/EC electrolyte are sufficient to form an interfacial layer with higher resistance to dendrite penetration.[89]

d. Addition of metal ions to the electrolyte

Incorporating inorganic cations to the electrolyte is an effective strategy. Since inorganic cations have higher reduction potentials than lithium, they can be deposited forming alloy layers with lithium at preferential places. The formation of these alloys can prevent the formation of dendrites because the film grows more homogeneously. Some of the tested cations are: Sn$^{4+}$, Sn$^{2+}$, Al$^{3+}$, In$^{3+}$, Ga$^{3+}$, Cs$^+$, Rb$^+$ and Bi$^{3+}$. [90–94]

e. Surface modification

Two novel approaches attempted to suppress dendrite formation by modifying the substrate. Ryou et al. proposed to mechanically modify the surface of Li metal before cycling.[95] The idea consisted in creating minuscule holes on the electrode surface with the help of a micro-needle rod. With the use of this technique, the Li anode could be cycled with higher current densities (0.750 mA h at a C-rate of 7C). This is approximately 20 % higher than the maximum C-rate used for charge/discharge of untreated bare Li metal electrode. In addition, a higher cycling stability was also observed. The initial discharge capacity remained constant over 150 cycles for the case of the treated electrode. Contrary, without treatment it lasted only for 70 cycles. [95]

Furthermore, the design of current collectors has also shown that it is possible to grow a more homogeneous film if lithium is deposited on a 3D-structured substrate. The technique consisted in the electrochemical preparation of a submicron Cu skeleton on top of a Cu foil. It provides a 3D porous structured current collector which could be used to grow homogeneous Li film. The high surface area of the substrate is optimal to improve the morphology because the charge transfer resistance is reduced. Thereby, the short circuiting of the battery due to dendrite formation is retarded to 600 hours. [67]

f. Modification of the charging protocol

Modification of the charging protocol in secondary electrodes has demonstrated to be beneficial for Zn metal anodes operating in aqueous electrolyte (see section 2.2.1). In lithium-ion batteries, pulsed charging was also implemented.[20, 96, 97] Although an enhanced cycle life was reported, the results are not related to the mitigation of Li dendrites (Li-ion batteries do not contain metallic Li). Both cathode and anode are affected positively in different manners. The structural damage of the cathode material interface is prevented. It is known that by cycling the cathode with a continuous current, the changes in the volume of the material produce internal cracks at the interface. Morphology studies of cathode materials, e.g. LiCoO$_2$, suggested that the concentration polarization is lowered with the introduction of relaxation times during
the charging process, since lithium ions have the time to diffuse. Therefore, the extraction and reinsertion of Li$^+$ ions are done in a more uniform manner.\cite{96} On the other hand, the anode also benefits with an intermittent charging protocol, since a thinner SEI layer is formed. \cite{20, 97}

More recently, simulation has shown that the charging protocol has a significant influence on the morphology of Li-metal anodes. The results indicated that the diffusion of ions also govern the dendrite formation of lithium in organic electrolyte. The application of short pulses favors the cation diffusion over reductive cation deposition at the anode interface. Therefore, these simulations indicated that dendrite formation might be inhibited. \cite{71, 72} This idea was experimentally confirmed by Yang et al. using scanning electrochemical microscopy to monitor the morphology changes of a bare lithium electrode.\cite{98} They found that applying a constant current density results in needle-type structures leading to dendrite formation, while smoother morphologies were achieved with pulsed charging protocols.
2.4 Morphology characterization

2.4.1 Scanning Electron Microscopy (SEM)

Scanning electron microscopy is nowadays one of the most useful techniques to characterize the morphology of a sample after electrochemical deposition. Electrons are emitted from an electron gun with high-energy and, then they are accelerated towards the sample. The interaction between the electrons and the specimen leads to responses which contain information about the sample, e.g. topography or chemical composition. Therefore, depending on the energy of the electrons emitted from the specimen and the desired information, different detectors can be employed: Auger electrons, secondary electrons, backscattered electrons. Also, characteristic X-rays and cathodoluminescence signals can be detected. The main disadvantage of using this technique for morphology characterization is the limitation to 2-dimension images.[99] Further information of the real surface area of a sample is not possible to obtain. In the field of zinc deposition, it is often employed to observe the shape of the deposit. Samples are relatively simple to be prepared and imaged because they are conductive and stable under high vacuum. An advantage over other techniques is that results can be achieved in a short period of time. Nevertheless, it is necessary to consider that samples may be degraded by the beam.[67, 95, 96, 98, 100–102]

2.4.2 Atomic Force Microscopy (AFM)

The morphological properties of a material can also be studied with AFM. This technique belongs to the family of scanning probe microscopies and is based on the interaction of a sharp tip supported on a thin cantilever with the surface of the sample. The tip is scanned over the surface and the deflection of the cantilever, which occurs due to changes in the topography of the sample, is monitored with a laser beam. With this technique, it is possible to obtain 3-dimensional images with a resolution in the order of nanometers. The biggest advantage is that samples can be measured without using high vacuum and no pretreatment is needed.[103] However, a long time is required to analyze a sample. For metal electrodeposition, AFM is used to measure the roughness of the surfaces.[67, 76, 104]

2.4.3 Electrochemical Impedance Spectroscopy (EIS)

The majority of techniques used in the evaluation of electrochemical reactions are based on the perturbation of the system either with direct potential or with direct current. The system response, either current or voltage respectively, changes over time depending on the deviation of the system from the equilibrium. Electrochemical Impedance Spectroscopy (EIS) changes from the dependency as a function of the time to a frequency dependency. In the potentiostatic mode, a given potential \(E_1\) is applied to the electrode. A sinusoidal signal with defined amplitude \(E_0\) and different frequencies \(\omega\) is superimposed [105]:
\[ E(t) = E_1 + E_0 \sin(\omega t) \quad (1), \quad \omega = 2\pi f \]

The phase shift and the current amplitude \( I_0 \) are measured at those frequencies:

\[ I(t) = I_1 + I_0 \sin(\omega t + \varphi) \quad (2) \]

The relation between the potential and the current, in direct current mode, is governed by Ohm’s Law \( (E=IR) \), where \( R \) represents the resistance for the current to flow through the system. In AC circuits, the impedance \( Z \) represents a measure of the opposition of a system to AC current. Therefore, impedance extends the concept of resistance to AC circuits.

EIS is considered a powerful analytical tool since it allows characterizing processes occurring at the electrode surface at different time scales. Any physical phenomena which takes place at the electrode interface can be interpreted with equivalent electrical circuit elements: resistors, capacitors, inductors. As it is shown in figure 8, the simplest circuit is composed of the ionic resistance of the electrolyte \( (R_e) \), the capacitance of the double layer \( (C_{DL}) \) and the charge transfer resistance \( (R_f) \).

![Fig. 8 Scheme of an equivalent circuit example explaining the process happening at the surface of an electrode at different time constants depending on the applied frequencies.](image)

The impedance is expressed as a complex function with a real and an imaginary component: \( Z(\omega) = Z_{Re} + Z_{Im}j \). The impedance of a capacitor has only an imaginary component, since the current and voltage are 90° out of phase. Equation (3) indicates that the impedance of a capacitor is dependent on the frequency.

\[ Z = 0 - \frac{j}{\omega C} \quad (3) \]
At the highest frequencies, the impedance of the capacitor is very low, behaving as a short circuit and becoming the preferential path for the current. As pointed out in figure 8, only fast processes at the electrode interface occur at high frequencies. On the other hand, at the lowest frequencies, the impedance of the capacitor tends to infinite, behaving as an open circuit and hindering the flow of current. Therefore, in this case the impedance of the cell is determined by the sum of the two resistors ($R_l + R_e$). Equation (4) shows that the impedance of a resistor does not have an imaginary component, since the current and voltage are in phase. Therefore, the impedance at low frequencies is associated with slow processes taking place at the electrode.

$$Z = R + 0j \quad (4)$$

A $Z''Z'$ plane is the most common representation (Nyquist plot) when evaluating the data. In this plot, every applied frequency has a corresponding $Z''Z'$ value. At high frequencies, most of the impedance derives from the resistance of the electrolyte ($R_e$). At low frequencies, the capacitor acts as an open circuit, therefore the impedance mostly derives from the resistors of the cell.

The previous discussion shows that qualitative and quantitative information can be extracted from an EIS spectrum. The use of EIS for the evaluation of zinc deposition has been limited to the study of inhibiting effect of additives on dendrite formation in alkaline media. It was found that PbAc$_2$ and tetra-n-butylammonium bromide (TBAB) have a similar effect in decreasing the capacitance of the double layer ($C_{DL}$) by a factor of four compared to the value obtained for an alkaline electrolyte without additives.[106] However, the interpretation of the entire spectrum and fitting to equivalent circuits is difficult, since several processes take place at the electrode. Another way of determining the capacitance of the double layer is based on the impedance at high frequencies. A more detailed explanation of this method is discussed in section 4.3.
2.5 Electrochemical secondary zinc cells

2.5.1 Type of Zn cells

a. Zn/MnO$_2$ battery

Metal Zn anodes were initially coupled with manganese (IV) oxide/manganese (III) oxide and, for many years, it has been the most commercialized primary battery.

$$
Mn_2O_3 + 2OH^- \rightleftharpoons 2MnO_2 + H_2O + 2e^- \quad E^\circ = -0.15 \text{ V vs. NHE} \quad (5)
$$

The recharge of this system remains as a major challenge. Manganese dioxide changes its structure and swells upon cycling. Silver powder was proposed as an alternative to mitigate this inconvenience. Nevertheless, the main drawback of the Zn-MnO$_2$ system is the formation of a non-rechargeable mixed Zn-Mn oxide phase.[2, 107] Metal oxide additives, such as TiO$_2$ and Bi$_2$O$_3$, can alleviate this problem, since they modify the physical structure of the mixture Zn-Mn oxide.[10]

b. Zn/AgO battery

Silver oxide presents many advantages as a rechargeable cathode coupled with the zinc metal anode such as high energy density and high C-rate capability. Silver can be oxidized to three different states: monovalent (Ag$_2$O), divalent (AgO) and trivalent (Ag$_2$O$_3$). In the rechargeable silver electrode, only in the mono and divalent forms participate (reactions (6) and (7)), since Ag$_2$O$_3$ is not stable in alkaline media [2, 10]:

$$2Ag + 2OH^- \rightleftharpoons Ag_2O + H_2O + 2e^- \quad E = -0.342 \text{ V vs. NHE, at pH 13} \quad (6)$$

$$Ag_2O + 2OH^- \rightleftharpoons 2AgO + H_2O + 2e^- \quad E = -0.607 \text{ V vs. NHE, at pH 13} \quad (7)$$

The high cost of this type of batteries makes it economically unsustainable and also not viable for testing at laboratory scale. However, for applications where high energy density is needed, this system represents an option to be considered. [108]

c. Zn/Air battery

The development of a secondary zinc/air battery has gained more interest over the last years due to its low cost, relatively simple technology and potential. This type of system represents an alternative solution to the electric vehicles market due to its high theoretically specific energy as well as stationary energy storage due to its low-cost. However, it has been difficult for researchers to propose a reliable rechargeable system.[109] In the positive electrode, the major challenge is to find an efficient and low-cost bifunctional catalyst for ORR/OER, which takes place via reaction (8).

$$4OH^- \rightleftharpoons O_2 + 2H_2O + 4e^- \quad E = + 0.401 \text{ V vs. NHE, at pH 13} \quad (8)$$

Besides the necessity of developing better catalysts, the improvement of a mechanically stable physical structure for the air breathing electrode is a critical issue from
the engineering point of view. Due to the low solubility of oxygen in aqueous electrolytes, the electrochemical reaction is limited to the three-phase boundary (solid-liquid-gas) requiring high specific surface areas. The design has to consider a compact thin electrode which includes at least active layers to retain the catalyst, a current collector and a microporous binder layer.[2, 4, 5, 110]

d. Zn/Ni battery

Another Zn-based battery that is attracting much attention is the Zn/Ni battery. Its high specific energy, extended life cycle (compared to other Zn-based batteries) and C-rate capability makes this system very attractive. This system delivers more than 1.5 V, which is significantly higher as compared to other consolidated aqueous cells such as NiMH which is limited to 1.2 V. Therefore, Zn/Ni may be effective for certain applications such as electric bicycles, scooters or trolling motors,[2] as well as stationary energy storage. At the positive electrode, nickel hydroxide \([\text{Ni(OH)}_2]\) is oxidized to nickel oxyhydroxide \([\text{NiOOH}]\) during the charging process following reaction (9):

\[
\text{Ni(OH)}_2 + \text{OH}^- \rightleftharpoons \text{NiOOH} + \text{H}_2\text{O} + e^- \quad E = + 0.49 \text{ V vs. NHE}, \quad \text{at pH 13} \quad (9)
\]

Both states, oxidized and reduced, have two different polymorphic forms: nickel hydroxide as \(\alpha\)-Ni(OH)$_2$ and \(\beta\)-Ni(OH)$_2$; nickel oxyhydroxide as \(\gamma\)-NiOOH and \(\beta\)-NiOOH.

---

**Fig. 9** Scheme of the two different polymorphs of Ni(OH)$_2$ and NiOOH. (II) and (III) represent the oxidation state of nickel. \(\beta\) refers to the form without H$_2$O or K$^+$ ions present in the crystal structure. Adapted with permission from [111]. Copyright 2006, The Electrochemical Society.
β-Ni(OH)\(_2\) is normally the phase of the discharged active material. In alkaline media α-Ni(OH)\(_2\) is not stable, therefore β-Ni(OH)\(_2\) is predominant. The α-phase does not participate during cycling. [112] When the electrode is overcharged for the first time, most of the conversion leads to γ-NiOOH. However, γ-NiOOH is electrically insulating and it is not possible to reduce the total amount of material. Therefore, β-Ni(OH)\(_2\) is oxidized to a mixture of β and γ-NiOOH in the subsequent cycle. Upon cycling, the proportion between these two phases (γ and β) becomes most favorable to β-NiOOH. [105, 113]

**Cell designs for the evaluation of the Zn/Ni system**

Studies of the reversible Zn/ZnO reaction have been carried out in different types of cells. In literature, it is uncommon to find an electrochemical cell with a third electrode to independently monitor the counter and working electrode reactions. Although some authors propose either Hg/HgO or metallic zinc as reference electrode, [18, 25, 27, 50, 59, 114–118] electrolyte-flooded cells were employed, in which case difference behaviors are obtained.

![Fig. 10](image_url) (a) Scheme and (b) photograph of three electrode electrolyte-flooded cell configuration for alkaline Zn/ZnO studies. The red circle shows the remains of the ZnO film.

To gain understanding of any electrochemical reaction it is essential to have a reliable cell. The electrolyte-flooded cell (see figure 10(a)) does not offer a reproducible geometry and the film is vulnerable to peel off and fall as it is shown in figure 10(b). In general, the overall behavior of an electrolyte-flooded and a battery-type cell are very different. In battery research, there are two main cell designs used to evaluate the electrochemical reactions: coin and Swagelok cells. [119, 120] The main benefit of standardizing the cells is to have the possibility of comparing results from different laboratories and to save time performing experiments without designing a specific cell every time a reaction needs to be evaluated.
In the field of Li-ion batteries, Swagelok T-cells offer several advantages over other systems. First, the T-shape of this cell allows inserting a reference electrode for separate monitoring of the potential at the positive and negative electrode. Secondly, the geometry of the cell is reproducible since electrodes have a known thickness and well-defined geometric area. They can be placed in the same position from one cell to the other. Thirdly, the close proximity between the working and the counter electrode improves the ion concentration gradient. Fourth, the electric contact and stability of the electrode films are significantly improved because electrodes are pressed one against the other, similar to the case in a commercial system. Therefore, electrochemical reactions can be properly evaluated at in-operando conditions with this prototype cell.

2.5.2 Reference electrodes for alkaline media

In the last decades, there has been a great effort to overcome the issue of the zinc negative electrode. However, the evaluation of the reversible reaction in a battery has been carried out in most of the cases in two electrode cells. In the best scenario, mercury/mercury oxide (Hg/HgO) was used as reference electrode in electrolyte-flooded cells because of its capability to measure potentials in high alkaline conditions. [60, 61] Nevertheless, HgO is soluble in alkaline media (6 mg/l in 6 M NaOH). If the electrode is not physically separated, the dissolved species can diffuse through the cell reaching the electrodes and leading to undesired reactions. Therefore, a porous membrane is commonly used to maintain the ionic contact while avoiding the mixture of solutions. Incorporating an additional compartment makes the design of the electrochemical cell more difficult. [121, 122]

Other authors reported the implementation of metallic zinc as third electrode. Zinc is known to be an excellent pseudo reference electrode for measurements in acidic conditions. Specifically, it is used to measure cathodic protection potentials in sea water because of the high concentration of chlorides. Nevertheless, at higher pH values Zn is not reliable anymore, since the metal is passivated and the measured potential is inaccurate. [50, 59, 114, 115]
2.6 Scanning Droplet Cell

The electrochemical analysis of small surface areas has been carried out by miniaturizing the components of the cell. In general, there are two ways of reducing the area of interest, either by decreasing the size of the working electrode (-microelectrodes) or by reducing the size of the entire cell (Scanning Droplet Cell). [123, 124]

Already in the late 70’s, the use of a small droplet of electrolyte was reported to perform localized electrochemical measurements on an aluminum surface. This idea was further developed and, years after, a tiny capillary was proposed to be filled with electrolyte, positioned inside the counter and reference electrodes. [125] The capillaries were initially made of glass (see figure 11(a) and 11(b)), but also plastic and metals have been used. [126] Nowadays, materials with hydrophobic property such as Teflon are used to define a reproducible working electrode area. [126–132] Normally, the opening of the capillary is in the range of 10 - 1000 µm depending on the application. Besides the miniaturization of the surface area, another advantage of this technique is the fact that only the area of analysis and not the entire sample have to be covered by electrolyte. This can be important when the sample is not stable under the electrolyte conditions.

![Fig. 11 SEM pictures of (a) glass capillary and (b) capillary equipped with a silicone gasket. (c) Schematic representation of a surface scanned with a scanning droplet cell. Reprinted from publication[125], Copyright (2006), with permission from Elsevier.](image)

Different spots over the surface of a large sample can be analyzed with potentiostatic and galvanostatic electrochemical techniques. [126, 132] Currently, the droplet cell is often used in a scanning mode (see figure 11(c)). Either the cell or the sample is connected to step motor driven positioning elements, which move automatically and enable accessing different parts of the surface for evaluation. This powerful instrument has been used to investigate biological cells, surfaces of catalysts, alloys, polycrystalline materials, thin films and for local metal deposition. [50, 126, 132–137]
3 Aim of the work

The widespread use of fossil fuels has a severe impact on the environment due to the increase in global emissions of carbon dioxide (CO$_2$). A new sustainable energy system based on renewable energy sources is necessary to decrease the anthropogenic impact by e.g. vehicles, coal-fired power plants, ships and aircrafts on the environment. Next generation of high energy batteries will play a key role in the establishment of a new sustainable energy model. Most of these high-energy batteries rely on the use of metal anodes. This work aims to contribute to the development of reliable metal anodes focusing on Zn and Li electrodes which represent the two most promising systems in aqueous and organic media, respectively. Most of the efforts have been devoted to the former, extending the main conclusions to the latter.

The growth of metal dendrites upon cycling (discharge-charge) at metal anodes is the main factor leading to battery failure and safety issues which prevents the use of metal anodes in commercial rechargeable batteries. In-depth understanding of dendrite formation in metal anodes is the Achilles’ heel for their application in rechargeable batteries. The large number of variables involved in the reversible electrochemical process of a metal increases the complexity of its fundamental investigation. In literature, there are several ways of mitigating dendrite formation, ranging from employing special separators to the use of additives.

In the first part of this work, an electrochemical approach to mitigate or even prevent the dendrite formation is presented. In order to develop a suitable charging protocol for the electrode, a high-throughput methodology is established to deposit and characterize the films. This alternative methodology reduces the timeframe necessary to perform the necessary experiments.

In the second part, a three-electrode Swagelok cell is introduced for electrochemical studies of the Zn/ZnO reaction. In order to understand a battery material at in-operando conditions, the electrochemical cell must fulfill two requirements: i) it must have a reference electrode which allows monitoring the potential of the positive and the negative electrodes separately, and ii) it must possess a battery-type configuration which allows detecting issues at real conditions such as electrolyte depletion or influence of gas evolution. Electrochemical cells found in literature do not fulfill at least one of the two requirements. The proposed three-electrode cell allows us to observe several unexplained aspects in Ni-Zn batteries such as the influence of non-woven separators in the thermodynamic shift of gas evolution or demonstrating that the kinetics of this battery is limited by the Ni electrode and not by the Zn electrode. The results have demonstrated the capabilities of this new analytical tool for the study of the Zn/ZnO reaction.
The last part of this work aims on demonstrating that the fundamental knowledge gathered by the successful combination of SDC and EIS-analysis can be applied to prolong the life cycle of commercial Ni/Zn batteries. In addition, since the electrochemical deposition of a metal is governed by similar factors both in organic and in alkaline solution, the concept is extended to organic systems. The main purpose is to confirm that diffusion plays an important role in the formation of dendrites in real applications and that such phenomenon can be prevented using an appropriate charging protocol. The benefits of implementing a galvanostatic pulsed-DC protocol in a battery could be reflected in a significant reduction of the production costs of the cells, since the implementation of the concept to commercial batteries would be rather simple.

In summary, the motivation of the work was to understand the dendrite formation in metal anodes and propose alternative methods to mitigate or prevent its occurrence in order to prolong the cycle life of secondary Zn based batteries. An electrochemical strategy of preventing dendrite growth was successfully developed, optimized and implemented in Ni-Zn and Li-LiFePO$_4$ batteries.
4 Results and Discussion

Part 4.1- Mitigation of Dendrite Formation in Zn Electrodes by Controlled Pulse Electrodeposition

The scanning droplet cell was constructed by Dr. Kirill Sliozberg, Ruhr-Universität Bochum. Parts of the following section will be published: Garcia, G.; Ventosa E.; Schuhmann, W. “Complete prevention of dendrite formation in Zn metal anodes by pulsed charging protocols. A high-throughput study”

The electrochemical deposition of metals is a complex process governed by thermodynamics (surface energy), kinetics (charge transfer at the interface) and diffusion (mass transport) (see figure 12(a)). Since conditions far away from equilibrium are applied, deposits with complex shapes can be obtained, e.g. branches and dendrites. Dendrites are expected to grow on zinc electrodes due to the high rates at which the electrode is cycled.

Since the formation of Zn dendrite does not only promote side reactions (HER) and passivation of the active material but also results in the short-circuit of the cell, there have been a large number of attempts to prevent and block this preferential growth, ranging from the use of membranes to the addition of additives. In this chapter, we explore an electrochemical approach in order to control the morphology during zinc deposition. A pulsed intermittent charging protocol was developed considering the influence of the diffusion limitation of zincate ions and the nucleation step at the very early stages of the metal growth.

![Fig. 12 Schematic representation of the electrodeposition of zinc in alkaline media: (a) Diffusion controlled process. (b) Reduction of ZnO via dissolution of zincate ions.](image)

Since the reduction of ZnO to metallic Zn proceeds via dissolution of zincate ions (see figure 12(b)), which are actually reduced to metallic Zn, understanding and controlling the electroreduction of zincates was the main goal in this chapter. Fundamental studies of the nucleation and growth of zinc were carried out in both acidic and alka-
line medium. Measurements were performed using a scanning droplet cell (SDC) which is a high throughput methodology that allows accelerating the study. A small Teflon capillary with an opening of 1000 µm of diameter (see details in section 6.1.2) was used.
4.1.1 Preliminary analysis of the electrochemical deposition of zinc on a glassy carbon electrode in acidic media

Cyclic voltammetry was carried out in a diluted acidic ZnSO$_4$ solution (0.05 M), containing sodium sulfate (Na$_2$SO$_4$) in a concentration of 0.5 M as supporting electrolyte in order to gather basic knowledge about the electroreduction of Zn$^{2+}$. The pH value of the solution was adjusted to 3 with sulfuric acid (H$_2$SO$_4$). The corresponding electrochemical process takes place via the reaction (10):

\[ \text{Zn}^{2+} \text{(aq)} + 2e^- \rightarrow \text{Zn} \text{(s)} \quad E^\circ = -0.76 \text{ V vs. NHE} \quad (10) \]

Very small differences were observed in the five different performed experiments, as detailed in the cyclic voltammograms (CVs). These results can be attributed to the morphology of the current collector. Two processes are observed in the CV of figure 13(a): the reduction of Zn ions below -1.0 V vs. Ag/AgCl (3M KCl) and the re-oxidation to Zn ion above -1.0 V. The crossovers appearing at around -1.2 V and at -1.05 V indicate that the deposition of Zn on the surface of metallic Zn occurred at lower overpotentials than the deposition of zinc directly on glassy carbon. It should be noted that the cathodic process was diffusion-limited below -1.25 V.

Fig. 13 (a) Cyclic voltammetry and (b) potentiostatic chronoamperometry recorded on glassy carbon in a 0.05 M ZnSO$_4$ and 0.5 M Na$_2$SO$_4$ solution (pH 3). Potentials are reported versus a commercial Ag/AgCl (3M KCl) reference electrode.

All transient currents measured by means of potentiostatic chronoamperometry measurements followed the same trend (see figure 13(b)). The current density increased due to the increasing surface area (nucleation and growth of the Zn nuclei) until reaching a maximum, which occurred due to the depletion of zincates at the electrode surface. After that, the current gradually decayed, dictated by planar diffusion of the zincate ions.
Since the preliminary results obtained for the electrodeposition of Zn (figure 13) were comparable to those obtained at macroelectrodes, we concluded that the scanning droplet cell (SDC) was a reliable technique to study the electrochemistry of Zn.
4.1.2 Electrochemical deposition of zinc on a glassy carbon electrode in highly alkaline media.

There are different applications of metallic zinc in acidic media. For instance, electroplating is important for fields such as galvanization, metallurgy, electronics and catalysis. However, alkaline media is required for the use of zinc as the negative electrode in primary and secondary alkaline batteries. Therefore, it was necessary to consider that the chemical and electrochemical behavior of the material changed with the pH. At high OH⁻ concentrations, the Zn/ZnO reversible reaction proceeded via the formation of intermediate soluble zincates [Zn(OH)₄²⁻], as explained in section 2.1.

A glassy carbon plate was chosen as the working electrode for the study of fundamental aspects of the electrodeposition of Zn due to its stability in alkaline media and its larger overpotential for HER, compared to other carbon base materials such as e.g. graphite paper.

Diffusion of soluble zincates plays an important role since [Zn(OH)₄²⁻] ions are the product of the oxidation of Zn and the reactant for the reduction to metallic Zn, according to reactions (1) and (2). At early stages, Zn(OH)₄²⁻ ions are located near the current collector surface. During the reduction, Zn(OH)₄²⁻ ions are consumed to form metallic Zn nuclei. As the film grows, the deposition occurred preferentially at certain locations. The increase of the size causes the formation of two types of morphologies: antenna shape (dendrites) and flat shape. Dendrites with hemispherical diffusion of zincates grew faster than flat areas with predominant planar diffusion due to the enhanced mass transport in the former case (see schemes in figure 12).

![Graph showing potentiostatic current density transients](image-url)

**Fig. 14** Potentiostatic current density transients for the deposition of Zn onto glassy carbon in 12 M KOH + 1 M Zn(OH)₄²⁻ at different potentials.

Since the early stages of the electrodeposition further determine the evolution of the film morphology, the study focused firstly on the nucleation and growth processes under potentiostatic conditions. Current transients at different constant potentials ranging from -1.65 V to -1.85 V vs. Ag/AgCl/3 M KCl were evaluated (see figure 14). The transients displayed a similar tendency as in the case of deposition of zinc in acidic media, i.e. the increment of the current over time till reaching a maximum was
followed by a gradual decay due to diffusion limitation. In addition, a “noise” in the transient was observed a few seconds after applying higher overpotentials values, which indicated the evolution of hydrogen. The slow diffusion of zincate from the bulk of the electrolyte resulted in a low concentration of zincate at the interfaces promoting hydrogen evolution. Electrolytes with a lower concentration of \( \text{OH}^- \) (<12 M KOH) were also evaluated. However, the larger availability of protons even more promoted hydrogen evolution during zinc deposition.

The influence of the two main parameters governing the growth of Zn metal films, namely overpotential and time, were evaluated by combining SDC and SEM measurements. Figure 15 shows the SEM images from deposits that were obtained potentiostatically (between -1.50 and -1.95 V vs. Ag/AgCl/3 M KCl) for deposition times ranging from 0.1 to 10 seconds.

Different trends in the different rows can be discussed from the SEM images shown in figure 15. The most relevant for the study is the row one showing the results from a deposition time of 1 s. This row clearly showed that separate large nuclei have started to grow already at a deposition time of 1 s, regardless of the applied potential. These results suggested that short pulses are necessary for successful pulsed charging protocols, which will be explained later in this chapter. The potential was increased progressively from -1.50 to -1.95 V. The images displayed in figure 15 demonstrated that just a few seconds are sufficient to cover the surface with layers of Zn deposits. Moreover, at a very short deposition time of 0.1s, the density of nuclei increased with the
applied overpotential and the layers overlap. However, this trend is valid only until 1.85 V.

As previously discussed, the charging process in a Zn electrode is governed by the diffusion of zincate ions. The overpotential caused from the concentration gradient of zincates can trigger side reactions, i.e. hydrogen evolution, which is thermodynamically favored but is kinetically hindered. Figures 16(a) and 16(b) show potentiostatic deposition of zinc for periods higher than 10 s.

HER may have taken place at the Zn uncovered sites. The noise signal in the current transients in figure 16(a) can serve as an indication of gas evolving reactions taking place. HER was confirmed for longer pulse times (see figure 16(b)) since the current density was much larger than the theoretical one expected for a diffusion limited process of zincate reduction. According to the Cottrell equation, the current density should be around -60 mA cm\(^{-2}\) for a deposition time of 10 s. The additional current must originate from the HER. Actually, current values within the theoretical limits were only found for electrodeposition potentials below -1.60 V vs. Ag/AgCl/3M KCl (see figure 14). It should be noticed that changes in the pH value deriving from the counter electrode for longer deposition times might also contribute to the increased current density in figure 16.

\[ \text{Fig. 16} \] Potentiostatic current transients recorded in a 12 M KOH and 1 M Zn(OH)\(_4\)\(^{2-}\) solution for (a) 20 s and (b) 40 s. Potentials are reported versus a Ag/AgCl/3M KCl reference electrode.

Non-homogeneous and rough deposits were observed in the SEM micrographs (see figure 17) for continuous electrodeposition longer than 10 s. However, no signs of dendrites formation were found. The convection induced by HER was considered by some authors as an advantage to prevent dendrite formation [9] Nevertheless, this side reaction is absolutely undesired in a sealed battery system.
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Fig. 17 SEM micrographs of electrodeposited zinc on a glassy carbon surface at different overpotentials during potentiostatic electrodeposition for 20 s and 40 s. The magnification in all figures is of 2000 times.

Although the advantage of using a high-throughput technique like SDC may have been already noticed, it becomes imperative for the following section in which several parameters have to be evaluated to design an optimal charging protocol. In a basic pulsed-DC charging protocol, a minimum of three parameters have to be evaluated: (1) Amplitude of the deposition pulse; (2) duration of the deposition pulse and (3) duration of the resting time necessary to restore the concentration of zincates at the electrode surface (see figure 18(b)). In addition, one the correlation between them has to be evaluated, which makes it a tedious task to design even a simple pulse protocol.

Fig. 18 Schematic representation of the potential profile as well as the corresponding current and zincate concentration profiles during Zn electrodeposition. (a) Continuous; (b) by DC-pulses. Potentials are reported versus Ag/AgCl/3 M KCl.

The charging process in a Zn electrode (reduction) is usually carried out by applying a constant current (see figure 18(a)). However, more homogeneous films can be ob-
tained when a metal is electrodeposited by current pulses. Changes in the roughness were evaluated by combining SDC with atomic force microscopy (AFM) and scanning electron microscopy (SEM). Since many samples can be prepared on a small glassy carbon plate by using SDC, the use of this technique accelerated the morphological characterization with AFM and SEM.

The morphology of samples was initially evaluated by means of SEM. Figure 19(a) shows the formation of Zn dendrites while applying a continuous current pulse of -50 mA cm\(^{-2}\) for 150 s. On the contrary, relatively smooth films which lack dendrites were obtained by applying a simple pulsed-DC electrodeposition protocol consisting in a 5 s deposition pulse followed by a 5 s resting period (see figure 19(b)).

**Fig. 19** SEM micrographs of zinc electrodeposited on glassy carbon from a solution 12 M KOH and 1 M Zn(OH)\(_4^{2-}\) at a current density of -50 mA cm\(^{-2}\) for 150 s applying (a) a continuous pulse, and (b) a pulsed-DC protocol of 5 s deposition pulses with breaks of 5 s in between.

Although SEM can confirm the presence or absence of Zn dendrites, this technique is limited to two dimensional images. AFM was employed for a precise determination of surface roughness necessary to compare and optimize charging protocols.

**Fig. 20** AFM images of Zn films electrodeposited from alkaline media onto glassy carbon electrodes with 5 s of resting time between deposition pulses. The duration of the deposition pulses (-50 mA cm\(^{-2}\)) was 2, 5, 10 or 20 s until a charge of 7.5 C cm\(^{-2}\) was reached.
Figure 20 shows AFM images of samples with different lengths of deposition pulse performed at a constant current density of -50 mA cm\(^{-2}\). Extremely rough surfaces were observed for pulses longer than 5 s. Surfaces of samples prepared by applying a continuous current are not shown because the roughness of these samples exceeded the limits of our AFM.

The cross sections (see figure 21) of the AFM images in figure 20 clearly show the differences in roughness amongst the samples. Deposits obtained with 20 and 10 s pulses showed an enormously rough surface. The roughness of the film significantly decreased by diminishing the length of the deposition pulse to 5 s (denoted as the magenta line (▬) in figure 21). Surprisingly, a further decrease in the length of deposition pulse to 2 seconds (denoted as the blue line (▬) in figure 21) resulted to be detrimental for the surface roughness. This unexpected result clearly showed that other parameters, as well as the interaction between these parameters have to be taken into account.

![Fig. 21 AFM cross sections of Zn films electrodeposited as shown in figure 20. The duration of the pulses (-50 mA cm\(^{-2}\)) was 2 (▬), 5 (▬), 10 (▬), or 20 (▬) s with 5 s of resting time between the pulses until a charge of 7.5 C cm\(^{-2}\) was reached.](image)

Besides the amplitude and the length of the deposition pulse, the duration of the resting period and the interaction between these parameters needed to be investigated, together with strategies to achieve smooth Zn films. These additional strategies comprise the application of a high amplitude and a short pre-deposition pulse. The introduction of this step in the charging protocol aimed to achieve a high coverage of Zn nuclei, in order to prevent HER at the underlying carbon surface. Since a high amplitude of the pulse is necessary, the length of this step has to be very short to prevent complete depletion of zincate. Figure 22 shows the importance of implementing this step, which is influencing the early stages of the Zn deposition. The roughness was drastically decreased by implementing a 0.2 s pulse with a current density of -100 mA cm\(^{-2}\) as part of the pulsed-DC protocol.
4 Results and Discussion

Fig. 22 AFM cross sections of Zn films electrodeposited from alkaline media on a glassy carbon electrode with: (▬) a pulsed-DC protocol consisting of 2 s deposition pulse (-50 mA cm\(^{-2}\)) with 5 s of resting time between pulses. (▬) The same pulsed-DC protocol adding a pre-deposition step of 0.2 s at -100 mA cm\(^{-2}\). In both cases, the film growth was performed until a charge of 7.5 C cm\(^{-2}\) was reached.

The increased mass transport favored a faster growth leading to the formation of dendrites. The same remains true for the anodic process: a higher rate of dissolution promoted the appearance of dendrites. Therefore, the implementation of a short anodic pulse during the charging process preferentially promotes oxidization and possibly inducing an “electrochemical polishing effect” at the electrode surface. Thus, in addition to a nucleation step, an oxidation step of +100 mA cm\(^{-2}\) for 0.2 s was added in the 37th step of the pulsed-DC protocol.

Fig. 23 Measured AFM cross sections of Zn films electrodeposited from alkaline media on a glassy carbon surface with 5 s of resting time between the pulses. The pulsed-DC protocol consisted of a 2 s pulse (▬) at a current density of -50 mA cm\(^{-2}\), addition of an initial pulse of -100 mA cm\(^{-2}\) followed by a 2 s pulsed-DC protocol (▬). The last case an oxidation step of +100 mA cm\(^{-2}\) was added after the 37th pulsed-DC protocol of 2 seconds (▬). In all cases, the film growth until a charge of 7.5 C cm\(^{-2}\) was reached.
Cross sections from the AFM images of the resulting film were compared with that of the previously obtained samples (see figure 23). The roughness was very similar to the experiment where only a nucleation step was implemented. Therefore, this strategy did not further lead to smoother surfaces, most likely due to the fact that the height of the antennas was already small for the anodic pulse to have any effect.

In summary, these preliminary results revealed some interesting aspects about Zn deposition. First, a pulsed-DC charging protocol was beneficial for the growth of homogeneous and smooth films. Secondly, the evolution of hydrogen influenced the deposition when short electrodeposition pulses were applied, since areas of the current collector remain uncovered by Zn, thus leading to a preferential growth at other areas. Lastly, the larger Zn coverage which is important to prevent the HER can be achieved by applying a nucleation step of high amplitude shortening the duration prior to the growth of Zn films.
4.1.3  High-throughput evaluation of the morphology of zinc deposits

The complexity of the electrodeposition of zinc in alkaline media requires the use of a high-throughput electrochemical technique to find the optimal pulsed-DC protocols. On the one hand, the amplitude and duration of the deposition pulse determines the nucleation and growth mechanism as well as the depth in depletion of zincate concentration at the electrode surface leading to a diffusion controlled regime. On the other hand, the duration of the resting period controls the reestablishment of the zincate concentration. In addition, hydrogen evolution may be promoted during electrodeposition of zinc.

Morphological characterization techniques such as SEM and AFM do not possess intrinsically a high-throughput capability, therefore, their systematic use slows down the study. Consequently, a high-throughput methodology to assess the surface roughness of samples has to be established. In this section, electrochemical impedance spectroscopy is proposed to characterize films and correlate the different growth conditions with their morphology.

![Fig. 24](image)

**Fig. 24** (a) Equivalent circuit in which the preferential current path at high frequencies is represented. (b) Nyquist plot of two EIS spectra recorded for different zinc films.

This technique can be implemented in-situ to assess the film morphology directly after the deposition also making use of a scanning droplet cell. The double layer capacitance at the electrode surface can be estimated from EIS measurements. The electrochemical double layer acts as a capacitor since there is a difference of charge between the two phases (see figure 24(a)). For a given condition, the amount of charge stored varies according with the morphology of the surface, since the measured capacitance \( C \) is the product of the specific capacitance \( C_S \), which is constant at given conditions, and the electrode surface area \( A \) as is express in equation (5):

\[
C = C_S A \quad (5)
\]
This proportionality may be used as an approximate of the surface roughness. A sinusoidal perturbation is applied to the potential in a broad range of frequencies and the processes occurring at different time constants can thus be observed. In the present work, we focused on high frequencies at which only the resistance of the electrolyte and the double layer capacitor contribute to the impedance (see figure 25(b)).

Since the time constant of faradaic processes is relatively slow, these processes are observed at medium/low frequencies. If even lower frequencies are applied, the diffusion limitation process appears. In the Nyquist plot, this region is called “Warburg” and is characterized by a 45° slope for freely diffusing redox species. On the other hand, when the frequency is limited to values in the order of kHz, only faster processes such as charging of the double layer are seen. Due to the alternating polarization of the electrode, ions are attracted and repelled to/from the electrode surface, acting as an electrochemical capacitor. Charging of the double layer is represented as a capacitor CDL in the equivalent circuit (see figure 24(a)).

As shown in section 4.2, the formation of dendrites can be prevented by applying a simple pulsed-DC protocol. Since the roughness of the films deposited by applying a continuous pulse and a pulsed-DC protocol was very different (SEM images in figure 26(a) and 26(b)), these two samples were used to validate the approximation of the surface roughness by EIS measurements.
The impedance \(Z\) of a capacitor does not have a real component, and it varies inversely proportional with the frequency. The capacitance of the electrochemical double layer \(C_{DL}\) was calculated using the following equation (6).

\[
C_{DL} = -\frac{1}{2\pi f Z''}
\]

Since the first frequency is recommended to be ignored, in order to avoid start-up transients while small leakage through the faradaic path occurs, the second highest frequency of 21544 Hz was selected for the determination of the approximate surface roughness (see figure 25(a) and (b)). It should be noted that significant changes were not obtained when using the first or third highest frequencies.

**Fig. 26** Upper part: scheme illustrating increased capacitance for rougher surfaces. Bottom part: SEM micrographs of zinc electrodeposited on glassy carbon from a 12 M KOH and 1 M \(\text{Zn(OH)}_4^{2-}\) solution at -50 mA cm\(^{-2}\) for 150 s applying (a) a continuous DC and (b) a pulsed-DC protocol of 5 s deposition pulses with breaks of 5 s in between. The capacitances calculated form EIS measurements are inserted.

The sample with the rough dendritic surface prepared by applying a continuous pulse (see figure 26(a)) resulted in a higher capacitance value of 1.22 µF, in comparison with the value of 1.09 µF, which was calculated for the smoother sample prepared by a pulsed-DC protocol (Figure 26(b)). This result confirmed that higher capacitances are obtained for rougher samples due to the increased surface area. It also validated the use of EIS for in-situ approximation of the surface roughness, allowing a full high-throughput evaluation of the morphology of deposited zinc films. It should be noted that SEM and AFM analysis were also carried out on selected samples (see below). Hence, it is feasible to perform large number of measurements and assess multiple pulsed-DC protocols in a reasonable timeframe. Indeed, this high-throughput methodology allowed to evaluate more than 1000 samples.
For simplicity, the imaginary part of the impedance is used from here on as an approximate of the surface roughness instead of the capacitance. In this case, the higher the value of the impedance, the smoother is the electrode surface.
4.1.4 **Electrochemical deposition of Zinc on graphite paper in alkaline media.**

The strong alkaline media together with the cathodic operating potentials limit the selection of Zn-based battery components. Normally, metal foils are employed as current collector due to their high electric conductivity as well as their relative flexibility. Lead and bismuth foils were proposed to be excellent current collector for the zinc electrode due to their chemical stability in alkaline electrolyte and their high overpotential for the hydrogen evolution reaction.

In our case, graphite paper (GP) was chosen as a current collector for two reasons: feasibility in real batteries and relative roughness which allowed good adhesion of Zn deposits. In addition, it is also very stable in highly alkaline conditions. However, the most important criteria to choose GP was because it does not interfere with the morphology of the deposit as other metals do due to the formation of surface alloys.

As in glassy carbon, potentiostatic current transients of Zn electrodeposition at different potentials from -1.60 to -1.85 V were first recorded on GP (see figure 27). At potentials more cathodic than -1.70 V vs. Ag/AgCl/3 M KCl, the current density appeared to quickly reach a diffusion-limited regime. After 10 s, the current densities recorded at -1.70, -1.75, -1.80 and -1.85 V overlapped at around the same value of -55 mA cm\(^{-2}\). Interestingly, this value was very close to the theoretical one of -60 mA cm\(^{-2}\) dictated by the Cottrell equation. This indicates that the evolution of hydrogen is hindered using GP, in contrast to glassy carbon, in which values in the order of -150 mA cm\(^{-2}\) well above the theoretical ones were obtained.

![Fig. 27 Potentiostatic current density transients for the deposition of Zn on graphite paper at different potentials using 12 M KOH + 1 M Zn(OH)\(_4\)^2.](image)

A current density of -56 mA cm\(^{-2}\) as amplitude of the deposition pulse was selected for the galvanostatic charging protocols since it is a reasonable value for practical battery application, e.g. a Zn electrode with a mass loading of 50 mg cm\(^{-2}\) requires a current density of -30 mA cm\(^{-2}\) to be charged within 1 h (1 C).

The approximate roughness of films prepared by applying a variety of protocols was evaluated. First of all, the influence of the duration of the deposition pulse was evaluation.
ated with respect to the approximate roughness while keeping the duration of the resting period constant (5 s) (see figure 28(a)). A significant improvement was observed from the continuous deposition to the pulsed protocol (-4.5±1.3 Ω and -7.7 ± 1.0 Ω for continuous and pulsed protocol, respectively). However, no significant differences were seen between deposition pulses of 2 or 5 s. Then, the length of the resting time was evaluated. Figure 28(b) shows that the shorter the resting period, the smoother the electrode surface was (-10.8 ± 2.7 Ω for 5s/1s, ON/OFF pulsed protocol). This result was unexpected, as one could assume that the longer the resting time the higher the concentration of zincates at the surface and the smoother surface would be. However, zincates can diffuse around 25 µm in 1 s according to their diffusion coefficient of $3 \times 10^{-6}$ cm$^2$ s$^{-1}$, which should be enough to reestablish their concentration at the surface. Actually, spontaneous corrosion of Zn during prolonged resting periods could be the origin of the detrimental results observed for longer resting breaks.

Although small improvements in the approximate roughness were achieved by changing the durations of the deposition pulse and resting period, the introduction of a new step in the protocol appeared to be necessary to obtain even smoother surfaces. The early stages of the electrochemical deposition are known to be of key importance in the growth of a metal. The number of active sites where nuclei can grow increase with higher overpotentials. Having a large Zn coverage is beneficial not only to prevent HER on uncovered areas, but also to avoid the creation of a few preferential sites which may lead to the formation of dendrites. We investigated the influence of a pre-nucleation step in the pulsed-DC protocol on the approximate roughness of the deposit. Specifically, 48 different protocols (see figure 29), consisting of different nucleation steps (varying amplitude, between -84 and -224 mA cm$^{-2}$, and duration of the pulse from 0.5 and 2 s) added to four pulsed-DC protocols, (i) 5s/2s, (ii) 5s/1s, (iii) 2s/2s and (iv) 2s/1s (On/OFF), were studied. It should be noted that Figure 27 displays the average value as well as the standard deviation of at least 5
replicates. First of all, the introduction of the pre-nucleation step, regardless of whatever type was used, resulted in a lower approximate roughness which indicates the benefits of the pre-nucleation step (see the comparison between Figures 28(b) and 29).

In general, a pre-nucleation step combined with pulsed-DC protocols with a length of the deposition pulse of 2 s led to very low approximate roughness. The best value was obtained for a pre-nucleation step of -168 mA cm\(^{-2}\) for 1 s, followed by a pulsed-DC protocol of 2s/1s, ON/OFF. The value obtained for this protocol (-24.7 ± 1.9 Ω) was five times larger than that measured for continuous deposition (-4.5 ± 1.3 Ω).
4.1.5 **Confirmation of surface morphology by microscopy techniques**

According to the approximate roughness estimated from the EIS measurements, significant improvements in the morphology of the electrode surface were achieved by optimizing the pulsed-DC protocol. As discussed before, the roughness estimated by EIS measurement should be taken as an approximate requiring the confirmation by microscopy techniques. Three selected samples were characterized with SEM and AFM.

![SEM images of Zn films electrodeposited on graphite paper](image)

**Fig. 30** SEM images of Zn films electrodeposited on graphite paper from a solution of 12 M KOH + 1 M Zn(OH)$_4^{2-}$ by applying (a) one continuous pulse of 150 s at -56 mA cm$^{-2}$, (b) a pulsed-DC (2/1 s, ON/OFF, -56 mA cm$^{-2}$) protocol and (c) a nucleation step (-168 mA cm$^{-2}$ for 1 s) followed by a pulsed-DC (2/1 s, ON/OFF, -56 mA cm$^{-2}$) protocol. The electrodeposition conditions are given as well as the pulse protocols are schematically illustrated below each SEM image. The value of $-Z_{\text{Im}}$ from EIS is also provided. (n>10).

The SEM images (see figure 30) were consistent with the EIS measurements of these three samples. The roughness of the electrode surface, the lower imaginary part of the impedance, and the SEM images clearly demonstrated the mitigation of the dendrites by applying a pulsed-DC protocol, also revealing a more dense and homogeneous film for the optimal protocol. However, this technique is not suitable to discuss differences in roughness at a nanoscale. Consequently, AFM was also employed to complement the analysis. The roughness of the sample prepared by continuous deposition exceeded the limits of our AFM, confirming the results from SEM and EIS measurements. Figure 31 shows the AFM images as well as a cross section of the images taken from the samples prepared by pulsed-DC protocol (2s/1S, ON/OFF) and the optimal protocol which included a pre-nucleation step. The AFM images showed that the roughness at the nanoscale became smoother by introduction of the nucleation step, which was consistent with SEM and EIS measurements.
Fig. 31 AFM images of Zn films deposited on the graphite paper from a solution of in 12 M KOH + 1 M Zn(OH)$_4^{2-}$ by applying (a) pulsed-DC (2/1 s, ON/OFF, at -56 mA cm$^{-2}$) protocol and (b) nucleation step (1 s at -168 mA cm$^{-2}$) followed by the pulsed-DC protocol (2/1 s, ON/OFF, at -56 mA cm$^{-2}$). (c) Cross section of the two samples (a) and (b).
4 Results and Discussion

Part 4.2- Three electrode prototype battery for the evaluation of Zn alkaline batteries

The modification to the Swagelok cell was carried out in the mechanical workshop of the Ruhr-University Bochum. Parts of the following section are published in ref. [136]: “Garcia, G.; Ventosa E.; Schuhmann, W.; ChemElectroChem. 2016, 3, 592–597”.

The rechargeable Zn-air battery is a promising alternative system for energy storage. However, they did not have been commercialized yet because there are still some challenges at both the positive and negative electrodes. In order to enhance the performance of the negative electrode, the Zn/ZnO reversible reaction needs to be evaluated at in-operando conditions. However, the performance of a Zn-Air battery is often limited by the O₂ bifunctional air-breathing electrode which makes it difficult to gather in-depth understanding of the Zn/ZnO reaction in this battery systems. Instead, Ni(OH)₂/NiOOH is a mature and reliable reaction. Coupling a Ni electrode with a Zn electrode enables reliable studies of the Zn/ZnO reaction in alkaline media in a battery configuration.

As previously discussed in section 2.3, different types of electrochemical cells have been used to cycle the reversible zinc electrode. Most of them are not appropriate to evaluate the reaction at in-operando conditions because either no reference electrode was used, which prevents the potential of the WE and CE to be measured separately, or the reactions takes place in an electrolyte-flooded cell behaving differently than when operating in a battery configuration.

In this chapter, a new electrochemical cell design, based on a Swagelok T-cell for Li-ion batteries is presented. The Swagelok T-cell offers the possibility of including the highly desired reference electrode in a battery type configuration. This configuration offers some advantages like pressing electrodes against each other to maintain good electrical contact and stability of the porous film, to reduce the distance between the electrodes for fast diffusion of OH⁻. On the other hand, it introduces some other challenges, such as possible short-circuit or damages due to gas evolution.
4.2.1 Electrochemical cell construction

In this work, we modified a Swagelok T-Cell, adapting it for alkaline conditions at which Zn-based batteries operate. Two main modifications were made to the cell: first, the reference electrode was exchanged since a small piece of metallic lithium was used as a reference electrode for the evaluation of Li-ion batteries. Evidently, this approach was not possible in aqueous media since metallic Li reacts spontaneously with water. A small carbon stripe cloth covered with Ni(OH)$_2$/NiOOH was chosen as the reference electrode. The reference electrode holder had to be modified as well (see figure 32). The modified carbon cloth was soldered to a stainless steel rod which was embedded in a piece of PEEK, required to secure an air-tight seal in the Swagelok cell (Figure 32(b)). The carbon cloth stripe was sandwiched between the working and the counter electrode, with two separators on each side (see figure 33(b)).

![Fig. 32](image1)

Fig. 32 Reference electrode PEEK holder used in a Swagelok T-Cell for the case of (a) Li-ion and (b) Zn-alkaline batteries.

The second modification concerned the protection of the internal cavity walls of the cell body. A thin electrically insulating plastic cylinder was used to cover the walls and prevent internal electrical contact between the electrodes, since the walls were made of stainless steel. For a Li-ion T-cell, a bended thin foil (350 µm) of polyethylene terephthalate is commonly used (commonly abbreviated as PET and named Mylar®). However, this material was not resistant to strong alkaline conditions. Therefore, the body insulator was replaced by a polyether ether ketone foil (PEEK), which was not easily corroded in the presence of hydroxide ions.

![Fig. 33](image2)

Fig. 33 Schematic representation of the cross section of a three-electrode Swagelok cell for the study alkaline Zn/ZnO reaction. (a) Entire cell and (b) magnification of the electrodes zone.
4.2.2 Development of a reliable reference electrode for alkaline batteries

A reference electrode is necessary to monitor and record the potential of the electrodes separately. A reliable reference electrode has to fulfill a major requirement. Its potential must be stable over time. Ideally, it should also be non-polarizable so that a stable potential is maintained even when a small current flows through it.

The first attempt in the establishment of a reference electrode for our system was the use of metal/metal oxide wires. It is convenient to use a metal wire due to its mechanical properties: it is relatively malleable and flexible and it adheres easily to the rod holder. Two systems were explored: Ag/AgO and Cu/CuO. Figure 34 shows the open circuit potential (OCV) of both of them versus a Ag/AgCl/3M KCl reference electrode.

![Figure 34](image)

**Fig. 34** Open circuit potential measurements of Ag/AgO (blue) and Cu/CuO (orange) in 2 M NaOH versus a commercial Ag/AgCl/3M KCl reference electrode.

Unfortunately, none of these two systems was found suitable to be used in alkaline media. In the case of Ag/AgO, the electrode was left at OCV after the oxidation of a silver wire. After 24 hours, the color of the oxide had partially changed, indicating a partial dissolution. Silver oxide is not completely stable in the presence of hydroxide, as shown in the following reaction (11):

$$AgO + OH^- + H_2O \rightarrow Ag(OH)_3$$

Cu/CuO was found to be more stable. Nevertheless, the open circuit potential fluctuated by ± 15mV over a period of 20 h. Therefore, we continued the search for a better reference system.

Instead of using a metal wire, a paste electrode containing powder of an inorganic redox compound was explored as reference system. The paste electrode were brought to 50 % state of charge (SoC) (1:1, oxidized:reduced species) to obtain a stable potential. An electrode containing [Fe(OH)$_2$/FeO(OH)] was the first system to be
explored. However, iron hydroxide was not completely stable at highly alkaline media, which was confirmed by the change in the color of the solution.

Other inorganic compounds such as lithium iron phosphate (LFP) and manganese oxide (Mn₂O₃) were also studied. After bringing the paste electrode to 50 % state of charge, the open circuit potential was monitored (see figure 35). However, these two materials did not deliver stable potentials.

![Fig. 35](image)

**Fig. 35** Open circuit potential measurements of (a) MnO₂/Mn₂O₃ and (b) LFP/L₀.₅FP in 2 M NaOH versus a commercial Ag/AgCl/3M KCl reference electrode.

Finally, the Ni(OH)₂/NiOOH couple was tested. A piece of carbon cloth was covered with a paste film containing nickel hydroxide. It was electrochemically oxidized to 50% state of charge (SoC) according to the following reaction (12) (see experimental details in section 6.2.3):

\[
\text{Ni(OH)}_2 + \text{OH}^- \rightleftharpoons \text{NiOOH} + \text{H}_2\text{O} + e^- \quad E = +0.49 \text{ V vs. NHE, at pH 13} \quad (9)
\]

Figure 36 shows the evolution of the open circuit potential of the Ni(OH)₂/NiO(OH) reference electrode against a commercial Ag/AgCl reference electrode. At a lower concentration of OH⁻, the potential varies by less than ± 2 mV over 8 days. Therefore, it can be considered stable for the duration of the anticipated measurements. When the concentration of OH⁻ increased, the potential showed a slight decay. After 8 days, the open circuit potential was 6 mV below its initial value. It can be concluded that this system is stable under alkaline conditions and it can be used as reference electrode for studying the Zn/ZnO reaction.

![Fig. 36](image)

**Fig. 36** Open circuit potential measurements of Ni(OH)₂/NiOOH in 0.5 M NaOH (blue) and 2.0 M (orange) versus commercial Ag/AgCl/3M KCl reference electrode.
Figure 37 shows a scheme comparing the potential of three reference electrode systems Ni(OH)$_2$/NiOOH, Hg/HgO (20% KOH) and Ag/AgCl (3M KCl). The potential of all systems is given against the standard hydrogen electrode (SHE). The potential of Zn/ZnO is also shown.

![Scheme of the reference electrode potential values](image)

**Fig. 37** Scheme of the reference electrode potential values (in mV at 25 °C) relative to the SHE potential for the reduction of ZnO to metallic Zn at pH 13.

The location of the RE in the developed Swagelok T-cell was discussed above (section 4.6). It is sandwiched in between WE and CE in the Swagelok T-cell design for studies in alkaline media. The size of the reference electrode was optimized with the aim of reducing the disturbance over the current lines existing between CE and WE. The selected length was fixed to 120 mm in order to encompass the diameter of the other cell components leading to a symmetric design. Three different widths were tested as reported in Table 1.

**Table 1** Experimental conditions of the working, counter and reference electrodes used to optimize the size of the reference electrode

<table>
<thead>
<tr>
<th></th>
<th>Small RE</th>
<th>Medium RE</th>
<th>Large RE</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>RE Length (mm)</strong></td>
<td>120</td>
<td>120</td>
<td>120</td>
</tr>
<tr>
<td><strong>RE Width (mm)</strong></td>
<td>1</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td><strong>WE Loading (mg ZnO)</strong></td>
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<td>6.56</td>
<td>7.13</td>
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<tr>
<td><strong>WE Capacity (mA h)</strong></td>
<td>4.12</td>
<td>3.93</td>
<td>4.28</td>
</tr>
<tr>
<td><strong>CE Loading (mg Ni(OH)$_2$)</strong></td>
<td>40.31</td>
<td>42.98</td>
<td>41.36</td>
</tr>
<tr>
<td><strong>CE Capacity (mA h)</strong></td>
<td>8.06</td>
<td>8.60</td>
<td>8.27</td>
</tr>
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</table>

Cyclic voltammetry was carried out in these three cells to evaluate the current density of the Zn electrode (see figure 38(a)). The current line distribution was affected when a wide RE (4 mm) was used, since the RE blocks the space between the working and
the counter electrodes. On the other hand, the use of thin REs (1 mm) was not satisfactory due to its mechanical fragility. A compromise between mechanical stability and blazing of current lines between WE and CE was found for REs with 2 mm width (see figure 38(b)).

**Fig. 38** (a) Effect of the size of the reference electrode on the cyclic voltammograms of a zinc oxide paste electrode in 2 M NaOH solution saturated with zinicates; scan rate 0.01 V s⁻¹. (b) Schematic representation of the reference electrode.
4.2.3 Selection of current collectors for the Zn and Ni electrodes

The reduction of ZnO occurs beyond the electrochemical stability window of water, even at high \( \text{OH}^- \) concentration. The rate of the hydrogen evolution reaction (HER), during the ZnO reduction is limited by kinetics, which makes the exclusion of materials capable of catalyzing HER in the electrodes imperative.

Several materials have been used as current collector, e.g. Pb, Sn and Bi foils are the most commonly used materials found in literature, since these materials are excellent to avoid hydrogen evolution. Nevertheless, their use is limited because their environmental impact is tremendous.[30, 119] Carbon based materials, e.g. carbon cloth and graphite paper, are potential candidates for current collectors for the positive and negative electrodes since they are good electrical conductors while inhibiting the gas evolution reaction. Figure 39 shows the CV recorded in 0.5 NaOH aqueous solution using copper, carbon cloth and graphite paper as working electrodes. It should be noted that the oxidation of copper in alkaline media limited the upper potential to -0.3 V vs. Ag/AgCl (3 M KCl).

![Fig. 39](image_url)

**Fig. 39** Effect of the current collector on the cyclic voltammograms for water splitting in 0.5 M NaOH solution at a scan rate of 0.01 V s\(^{-1}\). Carbon cloth (purple line), carbon paper (orange line) and copper foil (blue line).

HER at a carbon electrode requires additional 400 mV overpotential to reach -50 mA cm\(^{-2}\) when compared to the Cu electrode. Therefore, graphite paper was chosen as a current collector for Zn electrodes.

Carbon cloth offers a higher flexibility and a stronger adhesion of the film, therefore, it was chosen for the Ni electrode. However, the preparation of the film by doctor blade technique did not lead to homogeneous and reproducible films. While this was not a critical issue for the counter reaction (Ni electrode), graphite paper appeared to be a better option again for Zn electrodes since paste electrode with reproducible mass loading and homogeneous thickness can be prepared by doctor blade technique when using graphite paper.
4.2.4 Three-electrode versus two electrode cell configuration

Since both ZnO/Zn and Ni(OH)$_2$/NiOOH reactions occur outside the stability window of the electrolyte, the control of the cut-off potential (limit) of the system is critical at both electrodes due to the possible hydrogen and oxygen evolution reaction.

Figure 40(a) shows the potential profile of a two-electrode cell using -2.2 V and 0 V vs. Ni(OH)$_2$/NiOOH as cut-off potentials for charge (oxidation of Ni(OH)$_2$ and reduction of ZnO) and discharge (reduction of NiOOH and oxidation of Zn), respectively. Note that all potential values were negative because the Zn electrode acted as WE. The specific charge capacity decayed rapidly (Figure 40(b)), resulting in capacities below 50 mA h g$^{-1}$ after only a few cycles. The source of the decay is commonly attributed to the failure of the Zn electrode.

However, the use of a reference electrode enables to follow the changes in the potential of working (Zn electrode) and counter (Ni electrode) electrodes separately. Figure 40(c) shows that Ni(OH)$_2$ turned to be the responsible electrode for the cell failure. During the first discharge (re-oxidation of Zn), the potential of the counter electrode dropped below -1 V vs. Ni(OH)$_2$/NiOOH, which indicated that the reduction of oxygen...
and water were occurring instead of the reduction of NiOOH during the first discharge. This phenomenon indicated that during the first charge (reduction of ZnO), Ni(OH)$_2$ was not completely oxidized to NiOOH at the positive electrode, and side reactions such as oxygen evolution must have occurred simultaneously. Consequently, there was not enough NiOOH to balance the oxidation of Zn during the next step.

After a few cycles, the Ni electrode became activated and the reaction Ni(OH)$_2$/NiOOH occurred with higher coulombic efficiency. By controlling the cut-off potential of the Zn electrode with a reference electrode, the true decay in the performance of the ZnO electrode can be followed (see figure 40(d)).
4.2.5 Activation of Ni(OH)$_2$.

The evolution of oxygen in the Ni(OH)$_2$ counter electrode is an unpleasant drawback in the evaluation of the reversible Zn/ZnO reaction. Two approaches were followed to tackle this issue. The mass loading of Ni(OH)$_2$ was significantly increased and the Ni electrode was pre-activated electrochemically before assembling the cell.

Figure 41 shows the potential profiles of ZnO/Ni(OH)$_2$ cells containing (a) similar mass loading in both electrodes, (b) double mass loading of Ni(OH)$_2$ and (c) a pre-activated Ni(OH)$_2$ electrode for similar mass loading in both electrodes. Since oxygen evolution and the nickel hydroxide oxidation occur at a similar potential, the most reliable way of determining whether oxygen was evolving was to evaluate the potential of the Ni electrode during discharge (oxidation of Zn and reduction of NiOOH). If oxygen evolved at the Ni electrode during its oxidation and the reduction of ZnO, there would be not enough NiOOH to compensate the re-oxidation of Zn and, therefore, the potential of the counter electrode would drop below -1 V vs. Ni(OH)$_2$/NiOOH during discharge.

By evaluating the potential of the Ni electrode (orange line in figure 41(a)), it can be concluded that significant amounts of oxygen were produced in every cycle when a similar mass loading of ZnO and Ni(OH)$_2$ were employed. On the other hand, if the loading of Ni(OH)$_2$ was significantly increased (see figure 41(b)), only a small amount of oxygen evolved during the first cycle. Thus, having a large excess of Ni(OH)$_2$ was critical for the proper evaluation of the electrochemical properties of Zn/ZnO, avoiding interferences derived from the counter electrode. A remarkable poor performance of Ni(OH)$_2$ was observed during the first few cycles when a pre-activated nickel electrode was used (see figure 41(c)).

![Fig. 41 Potential profiles of cells with: (a) similar mass loadings of Zn and Ni(OH)$_2$, (b) double mass loading of Ni(OH)$_2$ and (c) pre-activated Ni(OH)$_2$ (for similar mass loading) at a charge/discharge rate of C/2 for 15 min.](image)

The potential of the Ni(OH)$_2$ electrode dropped below -1 V vs. Ni(OH)$_2$/NiOOH for several cycles. After 3-4 cycles, oxygen was not evolving anymore and the overpotential of the Ni(OH)$_2$/NiOOH reaction (the difference in potential for the oxidation and reduction nickel) was significantly reduced. Thus, the activation of Ni(OH)$_2$ was bene-
ficial after a few cycles, since the conversion of nickel hydroxide into a stable oxidized phase, \( \beta\text{-NiOOH} \), occurred during the pre-activation. However, the sources of the poor performance during the first cycles for pre-activated Ni electrodes are still unclear.

The results showed that an increment in the loading of Ni(OH)\(_2\) induces a less significant evolution of gas during the oxidation process. Nevertheless, a thick film is not beneficial in other aspects. A thick film is poor in conductivity, since the particles of active material at the top of the film are poorly connected to the current collector. The stability is compromised by increasing the mass loading (optimization of thickness / mechanical stability needed to be performed). Finally, having a thick Ni electrode induces unbalances in the charge capacity in the system, and only a fraction of the charge storage capacity of the Ni electrode is used.
4.2.6 Influence of non-woven separators (NWSs)

Non-woven separators (NWSs) have been reported to hinder the growth of Zn dendrites across the membrane, becoming a simple and popular approach to improve the performance of Zn-Ni batteries. Consequently, the influence of NWS on the electrochemical behavior of Ni and Zn electrode using the developed three-electrode cell was investigated. Figure 42 shows the galvanostatic potential profile (at C/2 for 15 min) of the Ni-Zn three-electrode cell. In this case, two NWSs were introduced between the CE and WE in addition to the Whatmann separators. Also, it was guaranteed that the CE had double of the loading with respect to the WE.

![Image of potential profiles]

**Fig. 42** Potential profiles of the Ni/Zn cell with a mass loading of Ni(OH)$_2$ of 20.65 mg cm$^{-2}$ with NWSs at 0.5 C ($\pm$300mA g$^{-1}$ZnO), for 15 min.

Comparing the results displayed in Figure 42 with those of Figure 41, it is possible to observe that as expected the activation of the counter electrode during the first cycle was still occurring when using NWS. The phase transformation at the nickel hydroxide during the first cycle is the key factor which allowed to fully utilize the material in the next cycles. However, it was noticed that the overpotential of the Ni electrode decreased during charging which probably led to the evolution of a lower amount of oxygen. Hence, NWSs may be beneficial to mitigate the oxygen evolution reaction, thus increasing the coulombic efficiency.

In order to further investigate the influence of NWSs, two cells were cycled at a higher C-rate (1 C) up to 100% SoC (charge and discharge). These cycling conditions require higher current densities as well as full charge–discharge of the Zn electrode. Since full discharges were applied and complete reduction of ZnO to Zn occurred, the cycles were limited by the set of the cut-off potential of -2.0 V vs. Ni(OH)$_2$/NiOOH. Figure 43(a) shows that this cut-off was reached right after the reduction of the ZnO was complete when NWSs were employed (right after the plateau finished). However, the cut-off was not reached when the cell was assembled without NWSs and a second plateau was reached after the complete reduction of ZnO (Figure 43(c)). This second plateau corresponds to the HER, which was not visible in the case of NWSs. Therefore, it appears that HER was suppressed when using NWSs.
4 Results and Discussion

Fig. 43 Potential profiles of Ni/Zn batteries (a) with and (b) without NWSs at 1 C (± 600 mA g⁻¹ZnO). Cathodic (orange) and anodic (blue) specific charge (c) with and (d) without NWSs at 1 C, based on the weight of the Zn electrode.

The cathodic specific charge of the Zn electrode in a cell without NWSs (see Figure 43(d)) clearly shows that the potential at the negative electrode did not reach the cut-off. It remained constant at 600 mA h g⁻¹ (time limit of 1 h), while the anodic specific charge decreased from 500 mA h g⁻¹ to below 50 mA h g⁻¹ after 15 cycles.

Figure 44(a) shows the performance of another cell containing NWSs in which the Ni electrode was pre-cycled 6 times for 15 min at C/2 to be activated. Afterwards, the cell was cycled at 1 C up to 100% SoC (charge and discharge). The potential remained in the plateau corresponding to the reduction of ZnO (-1.75 V) for 30 min, and it dropped to the cut-off potential which was set to -1.85 V vs Ni(OH)₂/NiOOH. The potential of the Ni electrode remained close to 0 V vs Ni(OH)₂/NiOOH, which indicates that the evolution of oxygen is also minimized.
4 Results and Discussion

Fig. 44 (a) Charge/Discharge profiles of ZnO (blue) and Ni(OH)$_2$ (orange) vs the Ni(OH)$_2$/NiOOH reference electrode in a three electrode cell configuration using additional Freudenberg separators at 1 C (600 mA g$^{-1}$ZnO) and a pre-cycled CE. (b) Specific capacity upon cycling.

Unfortunately, the specific capacity of the tested cells was only in average one third of the theoretical value (see figure 44(b)), which is due to other important aspects such as dissolution and redistribution of ZnO. It is necessary to take into account that zinc oxide has a poor conductivity. Inevitably, the particles get disconnected during cycling.

The specifications from the manufacturer guarantee that NWSs have random distribution or lack of fibers orientation. This feature suppresses dendrite formation of zinc, which is the main reason for the use of this type of separation. In addition, it is known that these polymer membranes also have the function to serve as additional reservoir of electrolyte. They can keep the electrode wet since they are subjected to a special treatment with wetting agents during the production process. However, the analysis of the 10 first cycles of the cell (previously to uncontrolled dendrite formation) suggested that the NWSs have an additional advantage avoiding the evolution of gases at the electrodes.

4.2.6.1 Suppressing of the hydrogen evolution reaction (HER).

The use of zinc for rechargeable batteries is limited mainly by the morphology change upon cycling as well as the low conductivity of the discharged electrode (ZnO). Nevertheless, the previous sections have shown that other detrimental issues such as the parasitic consumption of charge can take place through the oxygen evolution reaction (OER) on the nickel electrode and the hydrogen evolution reaction (HER) at the zinc electrode. The most widely used strategy to hinder kinetically HER has been the use of additive such as PbO. The use of the Swagelok T-cell allowed us to study and understand the influence of the parasitic reactions (OER and HER) during the charge-discharge process.

An electrode consisting of a current collector (graphite paper) without active material (ZnO) was used in the cell in order to evaluate the influence of the NWSs on HER (Figure 45(a)). It should be noted that the electrolyte contained zincates (Zn(OH)$_4^{2-}$) so that the reversible Zn/ZnO reaction was still observed although the negative elec-
trode did not contain active material (Figures 45(a) and 45(b)). When using NWSs, two clear plateaus were seen at the negative electrode corresponding to the reduction of zincate (-1.82 V) and HER (-1.95 V). However, only one plateau was visible without NWSs, which indicates that both processes, reduction of zincates and HER, were occurring simultaneously. Therefore, HER was shifted to more cathodic potential occurring only after depletion of zincates in solution when using NWSs.

![Fig. 45](image-url) Potential profiles of a cell without ZnO at the WE side (a) using (b) not using the non-woven separators Freudenberg 700/30K, at a charge/discharge rate of C/2 for 15 min. Since, there is no active material at the working electrode, the C-rate is based on the nickel electrode.

The shift of HER towards more cathodic potential can be explained from a thermodynamic point of view. Since NWSs hinder the crossover of gas, the partial pressure of the gas increase in its corresponding compartment, e.g. the partial pressure of H$_2$ increases in the negative electrode compartment. According to the Nernst equation, the thermodynamic potential for oxygen and hydrogen evolution depends on the partial pressure of oxygen and hydrogen, respectively. In other words, when the partial pressure of a gas increases, it become more difficult to produce more gas (thermodynamic shift of the potential).

$$E_{HER} = E_{OH^-/H_2}^0 + \frac{RT}{nF} \ln \left( \frac{1}{P_{H_2}[OH^-]^2} \right)$$

$$E_{OER} = E_{OH^-/O_2}^0 + \frac{RT}{nF} \ln \left( \frac{P_{O_2}}{[OH^-]^4} \right)$$

In conclusion, parasitic reactions in a Ni/Zn cell have a strong influence on its performance. Non-woven separators do not only act as a physical barrier between the two electrode in order to prevent dendrite formation of Zn. In addition, the results demonstrate that the structure of the NWSs hinder the crossover of gas leading to an increased partial pressure of the gases in the individual compartments. Therefore, the thermodynamic potentials of oxygen evolution (E$_{OER}$) and hydrogen evolution (E$_{HER}$) shift towards more anodic and more cathodic values, respectively, which reduce the amount of parasitic reaction and increase the coulombic efficiency.
4.2.7 Electrochemical Impedance Spectroscopy

The use of a two-electrode cell configuration does not only impede monitoring the potential of each electrode separately, but also hinders extracting quantitative information using other electroanalytical methods such as electrochemical impedance spectroscopy (EIS). In a two-electrode configuration, the measured impedance represents the sum of the impedance of both electrodes, making it impossible to quantify the contribution of the electrode of interest. This limitation was surpassed by using a reference electrode. The charging procedure of the cells was interrupted in order to perform potentiostatic EIS measurements at different state of charge (SoC), i.e. 25, 50 and 75 % SoC (Figure 46). The cell rested at open circuit potential for 2 min before EIS measurements to reach equilibrium conditions. The range of frequencies was between 100 KHz and 10 mHz, with an AC amplitude of 10 mV.

![Figure 46](image)

**Fig. 46** Schematic representation of the charge/discharge potential profiles of ZnO (blue line) and Ni(OH)$_2$ (orange line) indicating the different states of charge (SoC) at which the EIS was performed during the reduction and oxidation at the negative and positive electrode, respectively.

Figure 47 shows the Nyquist plots of the first 10 consecutive cycles obtained for the ZnO/Zn electrode at 25 % SoC (after 15 min at 1C). The first interesting observation was the slope at low frequencies, which does not show a 45° slope for the Warburg region (Figure 47(a)). In literature, slopes below 45° have been commonly assigned to disturbed linear diffusion caused by the high roughness of the porous electrode (more semi-spherical or semi-cylindrical). When magnifying the high-medium frequency region (Figure 47(b)), two semi-arcs became visible. Upon cycling, the semi-arc at high frequencies increased in size while the semi-arc at medium frequencies decreased, giving rise to an isosbestic point.

Since EIS provides information about processes occurring at different time constants and the oxidation of Zn to ZnO proceeds in two steps via the formation of soluble zincates (Zn(OH)$_4^{2-}$), the two semi-arcs can be attributed to these two steps. Since the
oxidation of Zn is a faster process than the precipitation of the Zn(OH)$_{4}^{2-}$ species, the high and medium frequencies semi-arcs were assigned to the oxidation of zinc and to the precipitation of Zn(OH)$_{4}^{2-}$, respectively.

Fig. 47 (a) Nyquist plot of a ZnO electrode for 10 cycles at 25 % SoC and (b) magnification of the high-medium frequency range.

It is also known that the dissolution of zincates from the Zn electrode is one of the main sources of capacity fading upon cycling (Figure 44(b)). The dissolution indicated an increase of the concentration of zincate, making their easier precipitation and leading to a decrease in the size of the corresponding semi-arc. At the same time, the high concentration of zincates might hinder the oxidation of Zn which makes the corresponding semi-arc larger (higher frequencies).

The impedance of the positive electrode was also measured at the same state of charge (SoC) as the negative electrode. Figure 48(b) shows the Nyquist plot of the first 10 cycles of Ni electrodes at 50 % SoC within the same range of frequencies used for the Zn electrode, (100 KHz -10 mHz). The EIS spectra of the first cycles (yellow-orange scattered points) showed a semi-circle at medium frequencies, which increased progressively upon cycling. After the fourth cycle (orange to blue) an additional charge transfer resistance at low frequencies became visible. This emerging charge transfer resistance at low frequencies can partially be attributed to the appearance of oxygen at the positive electrode, which was generated during charging (oxidation of Ni(OH)$_{2}$) at the Ni electrode.

A comparison between the EIS spectra of the negative and positive electrodes (see figure 48), revealed that the impedance of the Zn electrode was much lower than the one observed for the Ni electrode.
Against common belief, these results show that kinetics of a Ni/Zn battery are limited by the Ni electrode due to its much larger overall charge transfer resistance. In the previous section, polarization curves of figure 44(a) showed that the reversible reaction (oxidation/reduction) at the Zn electrode required lower overpotentials than that of the Ni electrode, which is also consistent with the EIS measurements. The two-step electrochemical reaction of ZnO/Zn proceeding via dissolution of zincate likely facilitates the reversible reaction compared to the intercalation process occurring at the Ni electrode.

**Fig. 48** Evolution of EIS spectra represented as Nyquist plots of (a) the Zn electrode and (b) the Ni electrode at 50% SoC over the first 10 electrochemical cycles. A magnification (8 x 8 Ω) of figure 48a is inserted into the same figure.
Part 4.3- Application of intermittent charging protocols to commercial Ni/Zn batteries and prototype Li-cells

Some experiments concerning the investigation of zinc and lithium deposition were obtained with the assistance of Osemudiamen Amedu, Stefan Dieckhöfer and Gemma Maskell, Ruhr-Universität Bochum, during student projects. Parts of section 4.15 are intended to be published: Garcia, G.; Ventosa, E.; Schuhmann, W. “Complete prevention of dendrite formation in Zn metal anodes by pulsed charging protocols. A high-throughput study”. Parts of section 4.16 are intended to be published: Garcia, G; Ventosa, E; Schuhmann, W. “On the road to the implementation of lithium metal anodes in rechargeable batteries through pulsed charging protocols”

In Part 1 of this work, the successful combination of SDC and EIS-analysis enabled a high-throughput evaluation of the influence of different parameters on the morphology of the Zn film. In this last part, the fundamental knowledge about the Zn dendritic growth, obtained by means of SCD/EIS, was employed to prolong the cycle life of commercial Ni/Zn batteries.

As in zinc electrodes, other metal anodes like lithium suffer from a change in the morphology upon cycling. The growth of a dendritic forest in the Li metal anode limits the possibility of using such kind of batteries for high energy-density purposes. In the last part of this chapter, the use of pulsed-DC protocols was extended to metallic Li deposition in organic electrolyte. The concept of the pulsed-DC charging protocol was applied to the Li-LiFePO$_4$ battery leading to outstanding cycle life exceeding 2000 cycles (and ongoing).
4.3.1 Recharging commercial Zn/Ni batteries by pulsed-DC protocols

4.3.1.1 Pulsed-DC charging protocol

The use of pulsed-DC protocol for electrodeposit of metallic zinc is a strategy that was shown in the previous sections to be effective in preventing dendrite formation. In order to apply this fundamental knowledge and demonstrate the benefits of the pulsed-DC protocol in batteries, the influence of the charging procedure on the cycle life of commercial AAA PowerGenix Ni/Zn batteries was evaluated. The performances of the battery cycled by three different charging procedures, i.e. a standard continuous charging and two pulsed-DC protocols, were compared. The batteries were cycled at 400 mA, since the manufacturer of the Ni-Zn battery recommends C-rates between 1–0.5 C for optimal performances and a PowerGenix AAA possesses a charge storage capacity of 545 mA h.

![Pulsed-DC protocol](image)

**Fig. 49** (a) Schematic representation of the charge/discharge pulsed-DC protocol applied to the commercial PowerGenix Ni/Zn battery from the second cycle on. Potential profiles of cells with a charge/discharge rate of 0.74 C at the: (b) 1\textsuperscript{st} cycle and (c) 10\textsuperscript{th} cycle. (d) Potential profile of the 10\textsuperscript{th} cycle of the cell with a charge/discharge continuous DC protocol of 300 mA. The voltage values are reported positive, since the Ni electrode acts as WE.
In order to activate the positive electrode, a continuous DC protocol was applied to all cells during the first cycle. The voltage profile corresponding to the first cycle of the cell is depicted in figure 49(b). The profile shows a particular shape during the first charge of the cell. Two plateaus were observed: the first one at ca. 1.9 V and the second above 2.0 V. The appearance of these two plateaus is related to the activation of the Ni electrode. During the first cycle, two phases of NiOOH (β- and γ-) are formed leading to the two plateaus in the voltage profile. The activation of Ni electrode consists in the stabilization of γ-NiOOH (Figure 49(c)) so β-Ni(OH)$_2$ is transformed to only γ-NiOOH in subsequent cycles. Since the potential of β-NiOOH is more anodic than that of γ-NiOOH (comparison of Figure 49(b) and 49(c)), more oxygen evolved during the first cycle. After charging the cell for 2.45 h, there was a sharp increase of the voltage up to 2.2 V, which indicated that all active material in one of the electrodes has been transformed. Since the activation of Ni electrode was completed after one cycle, the upper cut-off voltage for subsequent cycles was decreased to 2.0 V.

The charging process of the cell, represented in the voltage profile of figure 49(b), had duration of 2.45 h, while the discharge of the first cycle only lasts for 1.43 h before the potential drops to 1.2 V corresponding to the completion of the redox reaction. The difference of approximately 1 h between the charge and the discharge confirms that part of the charge was lost in irreversible reactions: O$_2$ evolution and H$_2$ evolution. Therefore, the efficiency of the first cycle is poor. After the first cycle, the battery was charged with a pulsed-DC (2/1 s, ON/OFF) protocol. The 10$^{th}$ cycle is depicted in figure 49(c). The modification of the charging voltage profile shows the short "spikes" in voltage derived from the pulsed current protocol (see figure 49(a)).

The influence of the charging protocol on the prevention of dendrite formation in a Ni/Zn battery was evaluated by cycling the cell until failure. The effects of the pulsed-DC protocol are clearly seen in the discharge capacity ($C_{\text{dis}}$) over the cycles. A rapid decay of $C_{\text{dis}}$ was observed when the cell was charged continuously, dropping below 25% of the theoretical value (136 mA h) during the first 10 cycles (Figure 50(a)). However, the discharge capacity was retained if a pulsed-DC (2/1 s, ON/OFF) protocol was used to charge the cell. In this case, $C_{\text{dis}}$ remained above 50% (272 mA h) and 25% (136 mA h) of the theoretical value for 275 cycles and over 500 cycles, respectively. The evolution of the coulombic efficiency upon cycling (Figure 50(b)) shows that i) the poor efficiency in the first cycle as discussed above and ii) the pulsed-DC protocol resulted in higher coulombic efficiency.
Fig. 50 Comparison between Ni/Zn PowerGenix AAA cells for continuous (orange) and pulsed-DC (blue) (2/1 s, ON/OFF) protocols, followed in both cases by a continuous discharge procedure. All of the cycles were performed at 400 mA. (a) Discharge capacity and, (b) efficiency upon cycling.

The SDC/EIS analysis of Zn electrodeposition (section 4.4) indicated that 2s/1s (ON/OFF) is the optimal pulsed-DC protocol (without adding additional steps like nucleation). For comparison, the influence of 5s/2s (ON/OFF) protocol on the cycle life of a commercial Ni-Zn battery was also evaluated. This protocol appeared not to have any beneficial effect on the cycle life of the battery since the charge storage capacity faded quickly as in the continuous DC protocol (Figure 51 (a)). The coulombic efficiency was poor with never exceeding 97%. Although SDC/EIS analysis anticipated a more homogeneous Zn film for 2s/1s (ON/OFF) protocol, such a big difference was not expected for the two pulsed-DC protocols. This fact suggests that the cycle life of a commercial Ni-Zn battery is very much affected by small differences in the deposition of Zn.

Fig. 51 Comparison between Ni/Zn PowerGenix AAA cells for continuous (orange) and pulsed-DC protocols: (2/1 s, ON/OFF) (blue), (5/2 s, ON/OFF) (turquoise). In all experiments the discharge procedure was done by applying continuous current. All of the cycles were cycled at 400 mA. (a) Discharge capacity and, (b) efficiency upon cycling.
The 2s/1s (ON/OFF) pulsed-DC protocol demonstrated to prolong the cycle life of commercial Ni-Zn batteries compared to the conventional continuous DC protocol at the same current density. However, introduction of resting periods prolongs the full charging protocol. As a result, pulsed-DC protocols require more time than continuous DC protocols when charged at the same current density leading to slower C-rates. Consequently, the performance of a Ni-Zn battery cycled by 2s/1s (ON/OFF) pulsed-DC protocol was compared not only to the continuous DC protocol at the same current density, but also to continuous DC protocol at lower current density (same C-rate). Another Ni-Zn battery was cycled applying a continuous DC protocol at 300 mA h. At this current density, the battery required 1.41 h to be fully charged which was the same time as the one which was charged with the 2s/1s (ON/OFF) pulsed-DC protocol at 400 mA (including the resting periods). The two batteries were cycled at the same practical C-rate of 0.7 C. When comparing the performance of the two batteries cycled applying the continuous DC protocol (Figure 52), one can see that slowing down the charging rate results in an increased coulombic efficiency, improved charge storage capacity and prolonged cycle life.

Nevertheless, after the 228th cycle a dramatic decrease in the $C_{\text{dis}}$ was observed, dropping values well below 50% of the theoretical value (272 mA h). Likewise, a drop in the coulombic efficiency to 98 % can be seen in the magnification of Figure 52(b) which occurred in the 229th cycle. Although higher current densities were applied with the pulsed-DC protocol, longer cycle life was obtained, i.e. 50 cycle more and 250 cycles more to fall below 50% (272 mA h) and 25% (136 mA h) of the theoretical value, respectively.

![Fig. 52 Comparison between Ni/Zn PowerGenix AAA batteries in pulsed-DC protocols of 2/1 s (ON/OFF) (blue) at 0.7 C (400 mA), and continuous DC protocols at two different C-rates: 1.24 C (400 mA in orange) and 0.70 C (300 mA in green). In all experiments a continuous current of ~400 mA was applied for the discharge process. (a) Discharge storage capacity and, (b) efficiency upon cycling](image)

In summary, significant improvement in the cycle life of commercial Ni-Zn batteries was achieved by applying a pulsed-DC charging protocol which derives from the prevention of dendrite formation and smoother Zn films obtained by this protocol.
4.3.1.2 SEM characterization of a cycled ZnO paste electrode

There are two difficulties in the evaluation of commercial batteries. First, the lack of a reference electrode limits the interpretation of results, since the potential of the positive and negative electrodes cannot be monitored separately. Second, these are sealed batteries and the electrodes are confined inside the casing. This complicates the post-mortem analysis of the morphology, since the dismantling of the cell may damage the electrodes.

In this section, an electrolyte-flooded cell was used to cycle a ZnO paste electrode in order to evaluate the influence of the charging protocol on the morphology of the electrode. The zinc electrode was cycled against a nickel electrode 10 times at a C-rate of 0.5 C, since large amounts of gas were evolved at higher current densities in the electrolyte-flooded cell compromising the stability of the electrodes. SEM images were taken for two ZnO paste electrode in the charged state (metallic Zn). Figure 53(a) and 53(b) show the film deposited after cycling the electrode with a continuous DC protocol and a pulsed-DC (2s/1s, On/Off) protocol, respectively.

![SEM micrographs of the ZnO paste electrode after 10 galvanostatic cycles at 0.5 C.](image)

The SEM images clearly show a remarkable difference of the surface morphologies of the two electrodes. Although small irregularities were observed in the zinc film cycled with a pulsed-DC protocol (Figure 53(b)), it was smoother and more homogeneous than the surface of the electrode cycled with a continuous DC protocol (Figure 53(a)). These images clearly demonstrate the importance of decreasing the roughness of the film in order to avoid the formation of dendrites and to enhance the life cycle of the cell.
4.3.1.3 Application of pulsed-DC protocols to other commercial cells

Different manufacturers of rechargeable Ni/Zn batteries are found in the market, e.g. PowerGenix, PKCell (China), UltraCell (UK), SCPS (France) and Conrad (Germany). In order to explore another alternative than PowerGenix, AAA Ni/Zn batteries from Conrad were purchased and tested. Although both cells have the same characteristics, AAA design, 900 mWh and 1.65 V, Conrad cells delivered improved performance when using a continuous DC protocol. Figure 54 shows that the Conrad cell lasted for almost 100 cycles above 25% of the theoretical discharge capacity (545 mA h) and the efficiency remain above 99% for almost 200 cycles.

Unfortunately, several cells were tested and no reproducible results were found, even though the cells were from the same batch. The lack of reproducibility prevented us to proceed further with the study of Conrad cells.

**Fig. 54** Comparison between two commercial brands of Ni/Zn batteries charged with a continuous DC protocol: PowerGenix AAA (orange) and Conrad (magenta). In addition results obtained from a charging pulsed-DC protocol of 2/1 s (ON/OFF) are shown in dark blue. In all experiments a continuous current of ~400 mA was applied for the discharge process. (a) Discharge storage capacity and, (b) efficiency upon cycling.
4.3.2 Control of dendrite formation in Li metal anodes by pulsed-DC protocols

A Li metal anode possesses the highest energy density of all battery materials. However, the dendrite formation upon cycling prevents its use in commercial devices. Therefore, much effort has been recently devoted to the development of a way of mitigating the lithium dendrite formation. Several strategies have been reported so far. Guo-Guo’s group prepared a 3-D copper current collector possessing high porosity and a skeleton structure. This type of electrode can accommodate the lithium inside as well as increase the surface area concomitantly decreasing the current density, and thus suppress the dendrite formation.[67] Another strategy proposed by Winter’s group is based on the mechanical modification of metallic lithium structure with a microneedle. They proposed to create a pattern on the lithium before cycling, so that the deposition takes place at those preferential sites, and then the electroplating could be controlled. As in the previous approach, the surface area of the patterned lithium electrode increases leading to decreased geometric current density.[95] Finally, a more electrochemical approach was presented by Whittingham. Their study suggests that with the application of an intermittent direct current it is possible to moderate the rate of lithium electrodeposition, which homogenizes the lithium film surface and decreases the roughness.[98]

4.3.2.1 Potentiostatic deposition of lithium on a copper foil

As for metallic zinc electrodeposition in aqueous electrolyte (see Part 4.1), the growth of lithium was first studied potentiostatically. Overpotentials from 10 mV to 640 mV were applied to electroplate lithium on a Cu foil. A Swagelok T-cell was used to perform the experiments in which two separate lithium foil pieces were used as the counter and the reference electrode. Figure 55 shows the current transients recorded from the potentiostatic measurements. For overpotentials below 160 mV, the current continuously increased over time (for 100 s) indicating that the deposition at those overpotentials did not reach the diffusion control regime. This type of slow electroplating leads to a more homogeneous film. Nevertheless, as was explained in Part 1, the practical application of these conditions is limited by the longer deposition time.

At overpotentials above 160 mV, the diffusion controlled regime was reached. The current rise due to the increase in surface area till a maximum was reached. At that moment, the concentration of Li-ions at the electrode surface was depleted and the process became diffusion controlled following a gradual decay of current as dictated by the Cottrell equation. The high deposition rates imply a faster depletion of the concentration of species near the electrode surface. Figure 55 also shows that higher values of the maximum current at shorter times were achieved with increasing overpotentials.
Results and Discussion

Fig. 55 Potentiostatic current transients for the deposition of Li into Cu-foil at different overpotentials, using 1 M LiPF$_6$ in ethylene carbonate/dimethyl carbonate (3:7 vol. %) with 2 %wt. vinyl carbonate as electrolyte. The overpotentials applied ranged from 10 mV to 640 mV.

The potentiostatic deposition of lithium at high overpotentials (>160 mV) was continued for periods longer than 100 seconds (figure 56) in order to promote the formation of dendrites and thus the short-circuit of the cell. At the highest applied overpotential of 640 mV, the cell was short-circuited at 116 s.

Fig. 56 Potentiostatic current density transients for the deposition of Li on Cu-foil at different overpotentials using 1 M LiPF$_6$ in ethylene carbonate/dimethyl carbonate (3:7 vol. %) with 2 %wt. vinyl carbonate as electrolyte. The overpotentials ranged from 160 mV to 640 mV.

The integration of the current density transients presented in figure 56 from 0 s until the time pointed with the arrows provided the amount of charge of deposited lithium before short circuit occurred. The amount of charge deposited at 640 mV was significantly lower (3787 mC/cm$^2$), since short-circuit of the cell took place after only 116 s. In contrast, at lower overpotentials, it is possible to increase the amount of deposited Li by as much as two-folds. These results demonstrate that the overpotential deter-
mines the growth of Li and the morphology of the electrode which are of key importance for the performance of a Li metal anode.

As previously mentioned in section 4.3.2, the evaluation of the morphology of the electrodes after cycling was not feasible with traditional post-mortem approaches since the process of removal of the separators modifies the morphology of the electrodeposited film. In order to preserve an unmodified morphology for SEM evaluation, the lithium film was grown at different conditions on the surface of a copper foil current collector using an open cell design (see section 6.3.3 for details).

Fig. 57 SEM micrographs of lithium electrodeposited on copper foil at 360 mV for three different periods of time: (a): 2 s, (b): 30 s, (c): 60 s. The electrolyte was composed of 1 M LiPF$_6$ in ethylene carbonate/dimethyl carbonate (3:7 vol. %) with 2 %wt. vinyl carbonate.

The ionic resistance of the open cell was 140 Ω higher than that of the Swagelok T-cell (approximately 10 Ω). Therefore, it was necessary to apply higher overpotentials to compensate the higher ionic resistance. An overpotential of 360 mV was chosen to evaluate the changes in the morphology at different deposition times (see figure 57).

The images of the potentiostatic deposition show that small lithium nuclei grew at very short deposition times. Two seconds were sufficient to have the surface completely covered. Deposition for longer times led to the formation of large lithium aggregates. It confirms that preferential growth of lithium in certain areas occurs for deposition times of 30 s. On the other hand, a relatively homogeneous and continuous film of Li was already achieved after 2 s.

4.3.2.2 Galvanostatic deposition of metallic lithium on copper foil

We investigated the influence of different pulsed-DC protocols on the amount of lithium which can be deposited before the Li dendrites short-circuit the cell. A current density of -20 mA cm$^{-2}$ was chosen, since this is a suitable value for real applications. For instance, a LiFePO$_4$ electrode with a mass loading of 30 mg cm$^{-2}$ would require a current density of -24 mA cm$^{-2}$ to be cycled at 0.2 C (5 h).
Figure 58 shows the potential profiles obtained by applying the different protocols. The arrow in the graphs indicates the time at which short-circuit occurred. The use of galvanostatic measurements for electroplating allows for a better control of the charge deposited, and a constant rate of growth over the entire experiment. The results presented in figure 60 show that as the duration of the pulses decreased, short-circuit was avoided for a longer time. Since the curves include the relaxation time, the amount of deposited charge has to be calculated for a proper evaluation.

A clear trend was observed after the calculation of the amount of electrodeposited charge. Table 2 shows a decrease of the charge until short-circuit of nearly 50% by shortening the length of pulse from 30 min to 7 s. More significant differences were found once pulses of 2 s were used. It was possible to deposit almost 3.5 times more lithium without any sign of short circuit than the amount deposited using a continuous DC protocol.
Table 2 Total deposition charge of the cells reported in figure 60. The calculation considered the deposition time until the cells were short-circuited.

<table>
<thead>
<tr>
<th>t_{dep} (s) (before short-circuit)</th>
<th>Charge (mC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Continuous-DC 1800s (On)</td>
<td>260 5876</td>
</tr>
<tr>
<td>Pulsed-DC 60s/5s (On/Off)</td>
<td>330 7458</td>
</tr>
<tr>
<td>Pulsed-DC 7s/5s (On/Off)</td>
<td>383 8656</td>
</tr>
<tr>
<td>Pulsed-DC 2s/5s (On/Off)</td>
<td>900 20340</td>
</tr>
</tbody>
</table>

The reduction of dendrite formation due to the application of pulsed-DC protocols was confirmed by means of SEM. As for the previous experiments presented in section 4.3.2, the lithium film electroplated in a Swagelok T-cell was peeled off during the removal of the separator. Therefore, the samples used for SEM characterization were prepared using the open cell design.

Films containing the same amount of lithium (2 mA h cm\(^{-2}\)) were prepared by applying four different electroplating protocols, i.e. continuous DC, pulsed-DC (60s/5s, ON/Off), pulsed-DC (7s/5s, ON/Off), pulsed-DC (2s/5s, ON/Off). The SEM images in Figure 59 show significant changes in the morphology among the four samples.

Fig. 59 SEM micrographs of lithium electroplated (2 mA h cm\(^{-2}\)) on a copper foil current collector. The electrolyte was composed of 1 M LiPF\(_6\) in ethylene carbonate/dimethyl carbonate (3:7 vol. %) with 2 %wt. vinyl carbonate. (a) Sample cycled with a continuous DC protocol. Samples cycled with a pulsed-DC protocol: (b) 60s/5s (On/Off), (c) 7s/5s (On/Off), (d) 2s/5s (On/Off). The magnification of all images is 350 times.
The preferential growth of lithium in some areas of the electrode is observed in the images of Fig. 59(a) and (b). Long deposition pulses (>7 s) favors the growth of rougher lithium films. Even discontinuities in the film became visible for long pulses. On the other hand, the morphology of the samples prepared with short pulses, i.e. 7 and 2 s (Fig. 59 (c) and (d), respectively) was more homogeneous, especially for the 2 s pulse profile. No particular area exhibited preferential growth. Therefore, the use of appropriate pulsed-DC protocols had a positive effect on the growth of a smoother film due to the reestablishment of the Li⁺ concentration during the relaxing period in combination with a short enough deposition time avoiding a diffusion-controlled regime.

4.3.2.3 Galvanostatic cycling of a Li-Li cell

In order to evaluate the influence of a pulsed-DC protocol on the cyclability of Li metal anodes, symmetric Swagelok T-cells were cycled until an internal short-circuit took place. One of the cells was cycled with a constant current and the other with a pulsed-DC (5s/2s, On/Off) protocol. Li/Li cells containing two Whatmann separators were employed. However, only one Whatmann separator was used for the experiments showed in figure 60 in order to accelerate the penetration of the dendrites through the separators.

Short circuit of the cells, which was confirmed with a multimeter, occurred after several hours of cycling due to the preferential growth of lithium. The cell cycled with a continuous DC charging protocol had a shorter life, which was exactly 30 cycles less than the pulsed-DC (5s/2s, On/Off) protocol. These results suggested that the pulsed-DC charging protocol, which led to the growth of more homogeneous films, can prolong the cycle life of Li metal anodes.

![Fig. 60](image-url) Potential profiles of the Li electrode in a Li/Li cell cycled in an electrolyte composed of 1 M LiPF₆ ethylene carbonate/dimethyl carbonate (3:7 vol. %) with 2 %wt. vinyl carbonate, at -0.88 mA/cm² for 1 h. (a) continuous DC charging protocol and (b) pulsed-DC (5s/2s, On/Off) protocol. The voltage values are reported against Li/Li⁺ in 1 M Li⁺.
4.3.2.4 Galvanostatic cycling of Li-metal anodes

The Li metal / LiFePO4 system was chosen for the evaluation of the impact of pulsed-DC charging protocols on the cycle life of a Li metal anode based battery. LiFePO4 (LFP) was chosen as cathode material to ensure that the Li metal anode was the limiting factor since LiFePO4 is an extremely reversible systems operating within the stability window of the electrolyte.

![Diagram of LiFePO4 battery system](attachment:diagram.png)

**Fig. 61** Schematic representation of the three-electrode Swagelok cell used to evaluate the effect of pulsed-DC protocols on the cyclability of Li metal based batteries. Lithium iron phosphate was the active material used on the positive side of the cell.

Figure 61 shows the schematic representation of the system used to evaluate the Li-metal anode. LFP represented as “Li+ intercalation compounds” was the cathode and a small piece of metallic lithium was used as reference electrode. The experiments were performed in a Swagelok T-cell designed for the evaluation of Li-ion batteries (see details in section 6.3.1).

Commonly, the charging process of Li-ion batteries consists of the application of a continuous galvanostatic procedure, followed by a potentiostatic mode once the voltage reaches a certain value in order to avoid overcharging of the electrodes. Figure 62(a) shows the scheme of the continuous DC protocol applied to charge a LFP/Li cell, while the experimental voltage profile of one cycle from this procedure is shown in figure 62(c).
Fig. 62 Schematic representation of the (a) continuous DC and (b) pulsed-DC protocol used for (dis-)charging Li/LFP in a three-electrode Swagelok cell. Cell voltage \( (E_{WE} - E_{CE}) \) for (c) the cycle 51 of a cell charged by continuous DC protocol and (d) the cycle 10 of a cell charged by pulsed-DC protocol. In both cases, the cells were cycled at 1 C. LiFePO\(_4\) acted as working electrode. The electrolyte was composed of 1 M LiPF\(_6\) ethylene carbonate/dimethyl carbonate (3:7 vol. %) with 2 %wt. vinyl carbonate.

The scheme of the pulsed-DC charging protocol proposed in this section is presented in figure 62(c) as well as an experimental (dis-)charge voltage profile (Figure 62(d)). It is important to notice that the relaxation time was not included in the calculation of the cell efficiency.

Figure 63 shows the results of the long-term evaluation of the Li/LFP batteries. The first observation to be noticed in figure 63 is that the discharge capacity was low (<200 µAh) during the first 5 cycles for all tested cells using the pulsed-DC and continuous-DC protocol (high and low C-rate). The charge storage capacity increased for all cases during the first few cycles. After 30 cycles, the charge storage capacity stabilized at different values, depending on the protocol applied to the cell. The increasing storage capacity appeared to be associated with LFP, which was slightly activated.
The preferential growth of lithium not only leads to a potential short circuit of the cell, but also enhances the decomposition of the electrolyte. Thermodynamically, it is known that the electrolyte decomposition process takes place before lithium deposition. Actually, metallic lithium reacts spontaneously with the electrolyte. The rougher the electrode surface is, the more reactive towards the electrolyte becomes. In addition, the electrically insulating film formed on the surface of lithium (solid electrolyte interphase or SEI), which is responsible for preventing the continuous decomposition of the electrolyte, needs to be rebuilt every cycle if the morphology of the electrode surface changes (Figure 64). Therefore, changes in surfaces roughness upon charging leads to an increased decomposition of the electrolyte, which upon many cycles can lead to the failure of the battery (depletion of Li$^+$ or simply lack of electrolyte).

The improvement in the cycle life when decreasing the current density (or C-rate) can be attributed to the deposition of a smoother and more homogeneous film at lower current densities which results in lower consumption of electrolyte. Similarly, the
homogeneous film obtained by pulsed-DC protocols prevented the roughening of the electrode surface decreasing further the electrolyte decomposition. The dendritic growth of lithium was expected to be responsible for the battery failure represented in the drastic and rapid decay of the discharge capacity. However, the dead cells did not show a short circuit between the electrodes indicating that the consumption of electrolyte was the origin of the failure (see figure 63 and 64).

**Fig. 64** Schematic representation of the rupture of the SEI layer on a Li electrode due to the formation of a very rough surface which leads to fast consumption of the electrolyte.

The use of continuous DC protocols at low C-rates can retard the failure of the battery but it cannot prevent it. On the other hand, a truthfully prevention of dendrite formation can be achieved with the application of the pulsed-DC protocols. High C-rates (1 C) can be applied while the homogeneous growth of the film enhances the life cycle since dendrites and electrolyte decomposition are avoided.
5 Summary and Conclusions

The growth of three dimensional zinc structures at the negative electrode of a secondary battery is a process governed by the diffusion of zincates ions from the bulk of the electrolyte to the interface of the electrode. These dendrites are capable to grow faster than the rest of the film, since the availability of ions at the formed sharp features is larger. In the scope of this thesis, preventing the propagation of dendrites is efficiently addressed by enhancing the mass transport. The introduction of short relaxation periods during electroplating of Zn prevents the formation of Zn dendrites resulting in smoother films, since the concentration of zincate ions is re-established at the electrode surfaces avoiding the competition of neighbouring sites for zincates.

The successful implementation of a high-throughput methodology allows to deposit and characterize electrochemically different films, with the aim of finding optimal Zn electroplating conditions. The tedious task of exploring a large number of interconnected parameters affecting the electroplating is accelerated with the use of a SDC. The acquisition of data is faster and the human error is minimized since the experiments are automatized. Moreover, an in-situ approximation of the surface roughness is facilitated by means of electrochemical impedance spectroscopy. The use of the capacitance of the electrochemical double layer, $C_{DL}$, determined from the EIS spectrum, has proven to be a reliable parameter which could be used to evaluate changes in the surface area of a film. The results are confirmed with SEM and AFM measurements.

In addition, the introduction of a nucleation pulse (short pulse of large amplitude), which allows achieving high initial coverage of Zn nuclei, appears to be more important than the duration of the plating and resting pulses. The combination of an optimal nucleation step and a pulsed DC charging protocol results in smooth Zn films, preventing completely the formation of dendrites and discontinuities in the film.

Commercially available Ni-Zn batteries such as PowerGenix AAA (900 mWh) benefit from pulsed-DC charging protocols. The cyclability of a PowerGenix battery can be prolonged from a few dozen of cycles to several hundreds of cycles when (dis)charged at 400 mA h concomitantly slowing down the capacity fade rate. The insights gathered for Zn electroplating using a model system are valid for commercial
Zn anode based batteries. SEM characterization of the zinc oxide paste electrodes confirms that pulsed-DC charging protocols prevent the dendrite formation at the Zn electrode. The interest to the development of a reliable metallic Zn anode has grown over the last year, a step further will be to address gas evolution encountered during the charging period.

A three-electrode Swagelok T-cell for in-operando electrochemical studies of secondary alkaline batteries was presented for the first time. The usefulness of the information obtained with the presented cell was demonstrated with I) the study of the role of non-woven separators (NWSs) in the electrochemical behavior of Ni/Zn electrodes, and II) electrochemical impedance spectroscopy analysis of the individual electrodes. Surprisingly, the Ni electrode half-cell was limiting during the first few cycles for cells with or without NWSs. NWSs improved the performance of the battery by inhibiting oxygen and hydrogen evolution at the positive and negative electrodes, respectively. The inhibition of gas evolving reactions is suggested to originate from the shift of the onset potential of the gas evolution reaction. NWSs suppresses the crossover of gasses leading to an increase in the partial pressure of the gas, which in turn shifts the thermodynamic potential of the gas evolution reaction. The charge transfer resistance of the Ni electrode was significantly larger than that of the Zn electrode, indicating that the kinetics of the Ni/Zn battery are limited by the Ni electrode. The use of the three-electrode Swagelok cell is therefore recommended for studies of secondary alkaline battery systems in a three-electrode battery-type configuration.

An alternative method to enable the use of Li-metal anodes is presented. The fundamental study of the electrochemical deposition of lithium on a copper current collector reveals that the application of only small deposition periods are necessary to reestablish the diffusion layer and thus to counteract the primary mechanism for particle size dispersion, namely interparticle diffusion coupling (IDC). A minimum overpotential of 160 mV is required for potentiostatic lithium plating, and a faster failure due to internal short circuits is observed as the overpotential increases. Likewise, the growth of dendrites is decelerated with a pulsed galvanostatic deposition of short periods. SEM images evidence that large lithium aggregates and films with high roughness are deposited with continuous charging protocols and smoother films are achieved from pulsed-DC protocols.
The positive effect of pulsed-DC protocols in the cycle life of Li metal batteries is reflected in outstanding results. The battery has lasted for more than 2500 cycles. The acceleration of the electrolyte decomposition process leads to a rapid failure of batteries charged with a continuous protocol, the formation of a rough film led to sharp structures which perforate the SEI layer, thus enhancing the consumption of electrolyte. The growth of a smooth surface allows retaining the SEI layer intact over many cycles.

The significant enhancement in the cycling stability of the studied metal anodes demonstrates the capabilities of charging protocols to completely prevent dendrite formation. This is a contribution to the development of a reliable new generation of secondary battery systems, aiming to be implemented in devices which require high energy density.
6 Experimental Procedures

6.1 High-throughput studies of Zn films

6.1.1 Scanning Droplet Cell

Galvanostatic and potentiostatic deposition of metallic zinc was carried out by means of a Scanning Droplet Cell (SDC) (Figure 65(a)). The head of the cell (Figure 65(b)) consists of a small compartment made of poly(methyl methacrylate) (PMMA) with a capacity of 100 µl. In addition, the cell holds the counter and reference electrodes in the upper part. On the left side, there is an inlet for the electrolyte, which is pumped into the cell with a peristaltic pump.

A platinum wire of 0.25 µm of diameter (Goodfellow) was used as counter electrode and a miniature home-made Ag/AgCl/3M KCl as reference electrode. At the bottom of the cell a PTFE tip is located. This capillary is used as reservoir for the electrolyte with a defined geometry (additional specifications are given in the next section). Once the tip gets in contact with a confined area of the surface (working electrode), the electrochemical measurement is restricted to the opening of the tip which, in this case, has a diameter of approximately 1000 µm. Therefore, many experiments in small areas can be performed (figure 65(c)).

A sensor controls the force applied by the tip onto the sample surface. Once a value of 400±50 mN was reached, the electrochemical measurement was carried out. The movements of the cell across the working electrode are performed by step motors in the coordinates x, y and z. A custom-made software written in Visual Basic 6.0 controls the automatic pumping of the electrolyte and the movement of the cell in all directions.
The electrochemical measurements were performed by triggering a MicroAutolab potentiostat/galvanostat (Metrohm-Autolab). In addition, electrochemical impedance spectroscopy measurements were carried out with the same instrument, since it contains a FRA modul. EIS measurements were recorded potentiostatically at OCV in a range of frequencies between 50 kHz and 1 Hz.

### 6.1.2 Preparation of the PTFE tip

The tip of the SDC was made of poly(methyl methacrylate) (PTFE). This is a very stable material, both chemically and electrochemically. Additionally, the plastic deformation of the tip offers an advantage when a large number of experiments are performed. Although it may be slightly compressed from one experiment to the other, the geometry of the tip does not change significantly. The hydrophobicity of PTFE prevents spreading the electrolyte outside the capillary guaranteeing the formation of droplets with the same size from one experiment to the other. The RE and CE are placed in the upper part (see figure 66(a)).

![Fig. 66 Schematic representation of the PTFE tip used for the study of metallic zinc deposition with the SDC, (a) entire tip and (b) capillary. (c) Photograph of the opening of the capillary taken with a microscope (Olympus BX-41).](image-url)

A tip with a tiny hole at the bottom (<500 µm) was obtained from the mechanical workshop. A screwdriver with a diameter of 1000 µm was used to enlarge the opening of the capillary (see figure 66(b) and 66(c)). Afterwards, the tip was polished slightly with sand-paper 2000 grit (Starke Matador) in order to remove PTFE burrs. Once residues were eliminated, the tip was polished again to have the entire ring in the same plane (see figure 67). For this purpose, the tip was screwed to the head of the SDC and a force of 400 mN was applied while the polishing paper (262X lapping film, grade 1MIC, type F. 3M) moved in ±x and ±y direction. The tip was considered suitable to be used when the diameter difference between the inner and outer ring was not larger than 10 µm.
6 Experimental Procedures

6.1.3 Preparation of working electrodes

Two carbon based materials were used as working electrodes. Glassy carbon was used for the validation of the SDC and graphite paper for all other experiments. To clean and homogenize the surfaces, the working electrodes were polished with alumina powder (Buehler). A few drops of a suspension containing Al$_2$O$_3$ were released on top of a polish felt paper. Then the electrodes were moved on it in random directions. To finish, a felt paper free of alumina was used to remove the remains from the surface of the electrodes.

The glassy carbon plates (Sigradur® G HTW) were polished with a polishing wheel. Three grain sizes of alumina were used: 1.0 µm alpha, 0.3 µm and last 0.05 µm gamma in the mentioned order. Both directions of rotation, backwards and forwards, were used for 3 min in each case for every grain size and, finally, the electrodes were ultrasonicated in water.

On the other hand, graphite paper (SIGRAFLEX® Folie F02012TH 0,20x500mmx50m) was polished manually. Due to the flexibility of the material it was attached to a glass plate with double side tape (see figure 68(a)). In this case, the paper was initially cleaned with ethanol (technical degree) to remove impurities, such as grease. Subsequently, the surface was polished with 0.05 µm gamma Al$_2$O$_3$ to homogenize the entire area. Figure 68(b) shows in the upper part a freshly polished bare electrode and in the bottom a used graphite paper electrode.

![Fig. 67 Schematic representation of the process of polishing the PTFE tip](image)

![Fig. 68 (a) Scheme and (b) picture of the graphite paper working electrode used for the study of the metallic Zinc deposition with the SDC with and without samples.](image)
6.1.4 Electrolyte composition

The deposition of Zn film was carried out in two different electrolytes: acidic and alkaline. Firstly, 0.1 M ZnSO$_4$ (Sigma-Aldrich) was used as a precursor (pH~3). The solution also contained 0.5 M Na$_2$SO$_4$ (Sigma-Aldrich) as supporting electrolyte and a few drops of H$_2$SO$_4$ (Sigma-Aldrich) were used to adjust the pH value. Secondly, a solution saturated with zincates (1 M Zn(OH)$_4^{2-}$) was used as the precursor in highly alkaline (12 M KOH; J. T. Baker). This solution was prepared by adding ZnO in 12 M KOH (1 M Zn(OH)$_4^{2-}$) (AnalaR NORMAPUR®). All solutions were prepared with tri-distilled and subsequently deionized water (Millipore, Milli-Q).

6.2 Development of a three electrode cell for the study of Zn/ZnO reaction in alkaline media

6.2.1 Swagelok three-electrode cell configuration

The body of the cell was a Swagelok tube connector covered internally with a PEEK foil, 42x39 mm$^2$ sheet and 100 µm of thickness (Victrex Europa). This foil isolates the electrodes and separators from the metallic body of the cell. As shown in figure 32, two stainless steel rods of 12.6 mm diameter partially covered with PEEK were used to hold and connect the WE and CE. In the case of the WE, a single piece was used. However, in order to apply reproducible pressure between the electrodes, the CE holder rod was divided in two parts and a steel spring was placed in between. The holder of the RE is explained in section 4.7. The cell was tightly closed with swivel nuts. In order to guarantee complete sealing, PTFE rings were placed between the rods and the nuts.

The assembly of the cell started by adjusting the PEEK foil to the walls of the body of the cell. Then, the RE holder is introduced (previously, the RE was attached to the holder). After that, the WE rod was fixed, and the WE and CE were placed inside with the 4 separators in between. The order of the elements is shown in figure 33. Last, the CE rods with the springs were fixed. The sealing of three nuts was checked at the end. The cells were assembled in an argon-filled glovebox (MBraun). Oxygen levels were maintained below 0.5 ppm.

6.2.2 Fabrication of paste electrodes

The composition of the positive and negative electrodes was optimized experimentally following the guidelines given in literature. In order to prepare the pastes, the slurries were mixed with an ultra-turrax disperser (Ika). The mixing procedure was done at 4000 rpm, and consisted of 3 repetitions of 10 min with resting periods in between (also of 10 min). Immediately after the preparation, a graphite paper (SIGRAFLEX® Folie F02012TH 0,20x500mmx50m) current collector was cleaned with ethanol and the slurry was spread onto it using the “doctor blade” technique. The paste was left to dry and to evaporate the solvent. Afterwards, in order to obtain the final shape and
size of the electrodes, a 12 mm disk was punched out with a commercially available hole punch (Hoffmann).

**Zinc oxide paste electrodes**

In first place, a binder dispersion (PTFE/water) was prepared using 60% polytetrafluoroethylene PTFE (Sigma-Aldrich) and 2% Triton X-100 (AppliChem) in distilled water. It was kept under magnetic stirring overnight. Then, the slurry was obtained by mixing 93.5% ZnO (AnalaR NORMAPUR®), 2% PbO (Sigma-Aldrich) and 1.7% carboxymethyl cellulose (Sigma-Aldrich) with 2.8% of a PTFE/water dispersion. The final weight composition of the binder suspension components with respect to the rest of the paste additives was 0.15% Triton X-100 and 2.65% polytetrafluoroethylene. The slurry was spread onto the current collector in order to have a film with a wet thickness of 230 µm. The film was dried at 60 °C for 20 min and then left at room temperature overnight. With the previous procedure, an active material loading of ca. 4 mg cm\(^{-2}\) was obtained for 12 mm disk electrodes.

**Nickel hydroxide paste electrodes**

The composition of the positive electrode was 94% of Ni(OH)\(_2\) (Sigma-Aldrich), 1% SFG44 graphite (Timcal), 2% C65 carbon black (Timcal) and 3% binder solution. In this case, the binder was a dispersion of polyvinylidene fluoride (PVDF) (Solef S5130, Solvay) in N-methyl pyrrolidone (NMP) (Sigma-Aldrich) in a proportion of 25 mg of PVDF per mL of NMP. The slurry was spread onto the current collector adjusting the wet thickness of the film to 600 µm. In this case, the film was dried at 60°C overnight because of the nature of the solvent (NMP). The final loading of active material obtained for 12 mm disk electrodes was ca. 16 – 18 mg cm\(^{-2}\).

**6.2.3 Fabrication of the reference electrodes**

The electrodes were prepared electrochemically in a three-electrode cell using a Pt counter electrode (Goodfellow) and a commercial Ag/AgCl/3 M KCl as reference electrode (Metrohm).

**Metallic wires reference electrodes: Ag/AgO and Cu/CuO**

Ag and Cu wires of 0.25 mm (Goodfellow) were used to prepare the electrodes. The electrochemical oxidation was carried out in a 2 M NaOH solution (J. T. Baker). The wires were immersed into the electrolyte, oxidized (Figure 69(a) and 69(b)) and left at open circuit voltage while monitoring the potential.
Fig. 69 Potentiostatic current transients corresponding to the oxidation of silver and copper wires in 2 M NaOH.

**Paste reference electrodes. Li$_x$FePO$_4$, MnOx and NiOOHx**

The paste electrodes were prepared following the procedure explained in the previous section. The graphite paper was replaced by carbon cloth (sample from Bayer) because of its flexibility.

LiFePO$_4$/Li$_{0.5}$FePO$_4$

Lithium iron phosphate was prepared by mixing 85% of LFP (MTI Corp), 3.5% SFG44 graphite (Timcal), 3.5% C65 carbon black (Timcal) and 8% of PVDF binder (25 mg of PVDF per mL of NMP, Solef S5130, Solvay/Sigma-Aldrich). After the drying procedure, the electrode was oxidized electrochemically to half of its total charge in a solution containing 2 M LiOH (Sigma-Aldrich) and left at open circuit voltage while monitoring the potential.

M$_2$O$_3$/MnO$_2$

The manganese ions was electrochemically oxidized from Mn$^{3+}$ to Mn$^{4+}$ to obtain a reference electrode 1:1 of Mn$_2$O$_3$:MnO$_2$. The paste electrode was composed by 70% of Mn$_2$O$_3$ (Sigma-Aldrich), 20% C65 carbon black (Timcal) and 10% of binder PVDF (25 mg of PVDF per mL of NMP, Solef S5130, Solvay/Sigma-Aldrich).

Ni(OH)$_2$/NiO(OH)

The slurry was prepared with the same composition as the counter electrode (see previous section). Nickel hydroxide was electrochemically oxidized to obtain a reference electrode 1:1 of Ni(OH)$_2$:NiOOH as shown in figure 70(b). Since the electrode is oxidized to half of its total charge the stability of the reference potential was enhanced.
Fig. 70 (a) Schematic picture of the reference electrode holder used in a three electrode Swagelok cell for the study of the Zn/ZnO reaction. (b) Potential measured during the preparation of the Ni(OH)$_2$/NiOOH reference electrode during galvanostatic cycling.

To continue with the preparation, a thin strip of carbon cloth coated with Ni(OH)$_2$/NiOOH was cut and stuck to the metallic connection of the holder with Leit-C Conducting Carbon Cement (Plano). Later on, a small piece of Sn was soldered around the metallic upper part (see figure 70(a)).

### 6.2.4 Electrolyte and separators

Four separators were soaked with 300 µl of 2 M NaOH solution, deoxygenated with Ar and saturated with zincate ions. Two of these separators were glass microfiber filters (1823-090 Whatman GF/D, Sigma-Aldrich) and the other two were grafted non-woven wet laid polypropylene (700/30K Freudenberg). The order is shown in figure 33.

### 6.2.5 Other general details for the measurements

The galvanostatic cycling of zinc electrodes was carried out using a VMP-3 potentiostat (Bio-Logic) within potential windows from −1.0 V to −2.0 V and charge/discharge rates of 0.5 C and 1 C. Also, the EIS measurements were performed with the FRA modulus of the same instrument. The frequency range was 100 KHz - 10 mHz.
6.3 Evaluation of Li dendritic growth

6.3.1 Swagelok Three-electrode cell configuration

![Swagelok Three-electrode cell configuration diagram]

**Fig. 71** Cross section of the three-electrode Swagelok cell used for electrochemical evaluation of lithium batteries. (a) Entire cell, and (b) magnification of the electrode zone. (c) Scheme of the arrangement of the electrodes and separators inside the cell.

Electrochemical measurements for the study of dendritic growth of lithium were carried out in a three-electrode Swagelok cell (see figure 71(a), 71(b) and 71(c)).

6.3.2 Electrolyte and separators for the Swagelock cell

The glass microfiber filters (1823-090 Whatman GF/D, Sigma-Aldrich) separators were soaked with a solution 1 M LiPF$_6$ in ethylene carbonate/dimethyl carbonate (3:7 vol. %) with 2 %wt. vinyl carbonate (BASF). Two separators of 12 mm diameter were placed between working and counter electrode containing 150 µl of electrolyte. Additionally, two more separators of 10 mm diameter with 120 µl of electrolyte were placed from the top to avoid short-circuit with the RE. The final disposition of the separators is shown in figure 71(c).

6.3.3 Three-electrode open cell

The electrochemical deposition of lithium on the copper foil was carried out in an open electrochemical cell made of PEEK with a capacity of 500 µl (see figure 72(a) and 72(b). A piece of copper foil (Schlenk Metallfolien), which was fixed to the bottom of the cell, was used as working electrode (surface area of 0.196 cm$^2$). A thin stripe of lithium foil (Sigma-Aldrich) was used as reference electrode. The Li foil was located close to the WE to minimize the Ohmic drop. Another piece of lithium foil was used as counter electrode. It was immersed into the electrolyte and placed from the side of
the WE. 200 µl of 1 M LiPF₆ in ethylene carbonate/dimethyl carbonate (3:7 vol.%) with 2%wt. vinyl carbonate (BASF) were used as electrolyte solution.

**Fig. 72** (a) Scheme and (b) picture of the open cell setup used for the morphological investigation of lithium dendrite formation.

The potentiostatic deposition of lithium using an open cell was carried out with a Modulab potentiostat (Solartron Analytical) in a three-electrode mode. The distance between working and reference electrode was kept constant from one experiment to another. The electrolyte resistance was measured and the electrodes were adjusted before each measurement to obtain a resistance of ca. 150 Ω.

### 6.3.4 Fabrication of LFP paste working electrode

LFP electrodes were prepared following the same procedure as for the other paste electrodes (see section 6.2.2). The current collector used for this case was 15 µm battery grade aluminum foil (MTI Corp). It was cleaned initially with ethanol and afterwards with a concentrated solution 30% potassium hydroxide. Finally, the hydroxide was removed with sufficient distilled water. This procedure was performed to remove aluminum oxides from the surface. The weight composition was 76% of LiFePO₄ (Lithium FerrousPhosphate Nano Co-crystalline Olivine; Advanced Lithium Electrochemistry) 15% C65 carbon black (Timcal) and 9% binder (Dispersion 25 mg/mL PVDF/NMP). The film was dried at 80°C overnight. The final mass loading of active material for this electrode was ca. 3 mg cm⁻².

### 6.3.5 Counter and reference electrode

Metallic lithium foil of 0.4 mm of thickness and 99.9% trace metals basis (Sigma-Aldrich) was used as counter and reference electrode. The oxides of the surface were removed by scratching the surface with a plastic tube until the metal becomes shiny. The final shape of the CE was a 12 mm disk, which was punched from the foil with a commercially available hole punch (Hoffmann). Lithium foil was also used as RE. A small piece of ca. 5 mm diameter was placed into the upper part of the cell as shown in figure 72(a).
6.4 Commercial Zn/Ni batteries

Two types of commercial Zn/Ni batteries, i.e. Powergenix and Conrad (see figure 73(a) and 73(b)), were used for the evaluation of the pulsed charging protocols. The first one was a rechargeable Powergenix AAA NiZn battery. The technical specifications from the manufacturer report a nominal voltage of 1.6 V with a capacity equivalent to 526.5 mA h (900 mWh). The second rechargeable NiZn battery was a Conrad AAA having the same features as the AAA battery from Powergenix. Powergenix recommend charging with constant current at 1 C to 0.5 C.

![Fig. 73 Picture of the commercial Zn/Ni batteries used from two providers, (a) Powergenix and (b) Conrad. Small metallic connectors were soldered with Sn to the positive and negative electrodes in order to have a stable connection to the potentiostat cables.](image)

6.5 Galvanostatic cycling of Li-LFP and Ni-Zn cells

The galvanostatic cycling (GC) and electrochemical impedance spectroscopy (EIS) experiments of all batteries were carried out using a VMP-3 potentiostat (Bio-Logic).

6.6 Microscopy techniques used for morphology characterization

6.6.1 Scanning electron microscopy

The morphology of zinc and lithium deposits were investigated by a scanning electron microscope (Dual Beam TM 3D FEG; FEI). During the measurements, the chamber was maintained at about $6 \times 10^{-10}$ mbar and operating at 20 kV.

6.6.2 Atomic force microscopy

The roughness of the samples was investigated by tapping mode AFM in air (JPK, NanoWizard 3).
7 References


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