A reality check and tutorial on electrochemical characterization of battery cell materials: How to choose the appropriate cell setup

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Abstract

The ever-increasing demand for electrical energy storage technologies triggered by the demands for consumer electronics, stationary energy storage systems and especially the rapidly growing market of electro mobility boosts the need for cost-effective, highly efficient and highly performant rechargeable battery systems. After the successful implementation of lithium ion batteries (LIBs) in consumer electronics and electric vehicles, there is still a need for further improvements in terms of energy and power densities, safety, cost and lifetime. In the last decades, a large battery research community has evolved, developing all kinds of new battery materials, *e.g*. positive and negative electrode active materials for different cell chemistries, electrolytes, related auxiliary (inactive) materials and their constituents.

Different battery cell setups, including so-called "*half-cell*", "*symmetrical-cell*" and "*full-cell*" *setups* as well as *two-electrode* or *three-electrode configurations*, are described in the literature to be used in the laboratory for the electrochemical characterization of battery components like electrode materials and electrolytes. Typically, all cell setups display certain limitations or issues concerning their application for the parameter determination of battery materials. In this review article, we highlight the advantages but also the limitations of different cell setups, with special focus on *two*- and *three-electrode configurations with or without the help of "auxiliary" excess capacity Li metal electrodes*. We point out possible mistakes and/or misinterpretations and give the reader recommendations, *i.e.*, a guide for the right choice of the cell setup/configuration appropriate for the intended aim of the electrochemical investigation.

KEYWORDS

two-electrode configuration; three-electrode configuration; half-cell setup; full-cell setup; lithium ion batteries

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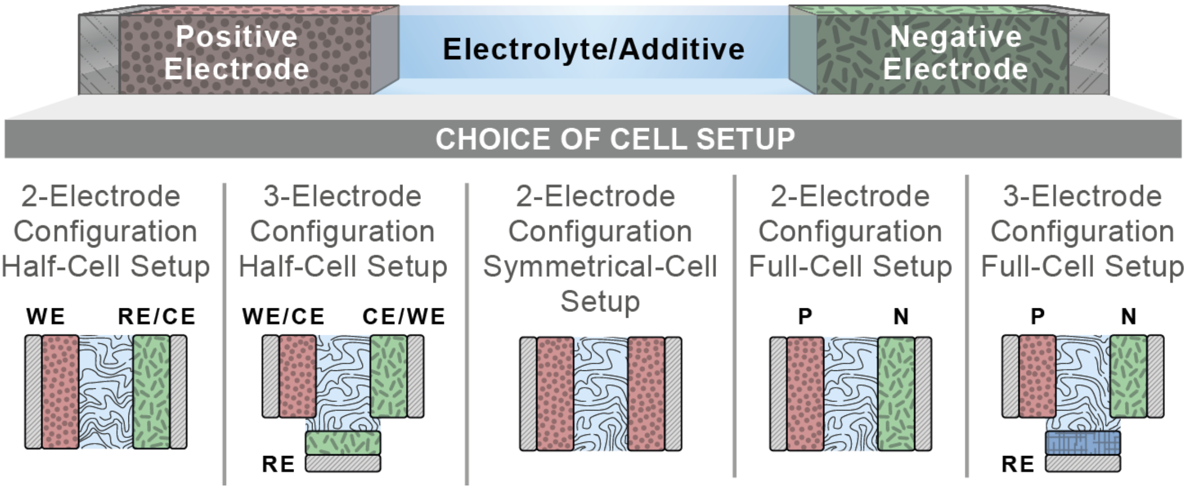

1. Introduction

The integration of clean renewable energy generation in combination with highly efficient and performant energy storage technologies is one of the major targets of the present energy economy. Currently, rechargeable batteries are widely seen as one of the most efficient and feasible storage solutions for specific application purposes, especially for mobile applications. The need for improved batteries is particularly boosted by the rapidly growing markets for electro mobility, industrial batteries, *etc*.[1] Nowadays, the lithium ion battery (LIB) technology is the most dominant technology for a variety of applications, which particularly include portable electronic devices, industrial applications, power tools, electric-powered bikes, scooters and automotives as well as grid (home) storage.[2-5] As depending on the type of application, there is a different prioritization of key performance indicators, *i.e.* of energy, power, lifetime, sustainability, *etc*., various material combinations for battery cell application have been investigated in the past and will be pursued in the future.[6-8]

Emerging battery technologies (*e.g.* lithium-sulfur (S || Li), lithium-oxygen (O_2 || Li), *etc.*) often promise a very high theoretical energy per volume or mass, however, these energy values often exclude numerous relevant parameters for practical battery cells, such as the practical mass utilization of the active material, practically achievable discharge voltages, as well as the required amount of inactive materials. As a consequence, the theoretical energy values that are commonly stated for these evolving battery chemistries might drastically overestimate the realistic potential of these systems in comparison to state-of-the-art LIBs. Thus, we recently reported on a novel method calculate the energy values of different battery technologies to give a more transparent and realistic assessment and comparison of current and emerging battery technologies.[9]

In order to develop advanced battery cell technologies, fundamental research studies on new cell components are mandatory. There are various electrochemical techniques and conditions, multiple and different cell components and cell types/setups to characterize a certain, new battery material or electrode of interest, which often makes it hard or even impossible to compare results of different studies with each other. Furthermore, an “inappropriate”, or even “wrong” selection of the cell components and/or measurement conditions may lead to a misinterpretation of the results regarding the material of interest.

In this review, we focus on electrochemical studies of battery components in different battery cell setups, *i.e.*, “*half-cell*”, “*symmetrical-cell*” and “*full-cell*” *setups* with special focus on *two-* and *three-electrode configurations*, where we specifically want to point out the advantages and limitations with respect to the desired target of research. Furthermore, we demonstrate possible mistakes and/or misinterpretations and give the reader recommendations for the suitable and "right" choice of the cell setup, appropriate for the intended aim of the electrochemical study.

2. Definitions: *Half-cell vs. symmetrical-cell vs. full-cell setup* and *two-electrode vs. three-electrode configurations* in battery research

Different cell setups used in battery research, namely *half-cell setups*, *symmetrical-cell setups* and *full-cell setups*, as well as the major differences between *two-electrode* and *three-electrode configurations*, are briefly introduced and discussed in this section. A schematical illustration of the different cell setups and configurations is given in **Figure 1**. In this article, we mainly focus on the lithium ion battery (LIB) technology, however, the general definitions and conclusions can also be transferred to other battery systems, such as lithium metal batteries (LMBs)[10,11], sodium-ion batteries, dual-ion batteries, O_2 || metal- and S || metal-batteries, *etc*. As like other battery cell systems, a classical LIB cell is composed of a negative electrode (N) and a positive electrode (P), which are mechanically separated by an electrolyte-wetted separator.[12] This *two-electrode configuration* is typically termed as "*full-cell setup*" in battery research (as depicted in **Figure 1 (d)**), in which the cell voltage, defined as the difference of the potentials of P and N, is used to control the charge and discharge cut-off conditions during constant current charge/discharge cycling.[13,14] In various reports, N and P are commonly named as anode and cathode, respectively. However, this designation is only valid when the electrochemical cell is used as a galvanic cell in the discharge mode.[15] In case of an electrolytic cell (=charge mode of the cell), P would be correctly described as anode, because anode and cathode are defined as the respective electrodes where oxidation and reduction occur, respectively.[16] Following the classical nomenclature[16], the conventional notation of a galvanic cell is given by notation (I). Examples for this conventional notation are the Daniell cell (copper and zinc electrodes), as illustrated by (II) or a classical LIB cell based on a graphite N and layered transition metal (*TM*) oxide P, as depicted by (III).

$X\|X^+ \;\|\|\; Y^+\|Y$	(I)	Galvanic cell
$Zn\|Zn^{2+} \;\|\|\; Cu^{2+}\|Cu$	(II)	Daniell cell
$Li_xC\|C + xLi^+ \;\|\|\; Li_{1-x}TMO_2 + xLi^+\|LiTMO_2$	(III)	LIB cell

Within this notation, N (where oxidation takes place during discharge/galvanic operation) is depicted on the left side and P (reduction during discharge/galvanic operation) on the right side, whereby the equations of the single half-cells (one vertical line) are separated by a double vertical line, representing a salt bridge (*e.g.*, Daniell cell) or a separator (*e.g.*, LIB cell).

However, due to simplicity, the most common description for LIB cells used in the battery research community is typically "P/N" or "P || N" (*e.g.*, $LiTMO_2$/graphite or $LiTMO_2$ || graphite). For simplicity reasons and better readability, we will solely use the latter simplified notation "P || N" in this article and also encourage the use of this notation for research articles.

The central object of consideration (the material or electrode of interest) in electrochemical studies is often placed on only one of the electrodes for reason of systematic research, *e.g.* with respect to evaluate the material properties for reversible ion storage, such as electrode potential, reversible and irreversible capacities, *etc*. To control and monitor the potential of the electrode of consideration independent of the other electrode, either a *two-electrode configuration* or a *three-electrode configuration* can be used. This setup is called *half-cell setup,* and in the following, the electrode of consideration in such potential-controlled cells will be named *working electrode* (WE; **Figure 1 (a)** and **(b)**), as it is common practice in numerous research papers and electrochemistry textbooks.[16] However, it has to be kept in mind that an accurate measurement of the WE potential in the *two-electrode configuration* (**Figure 1 (a)**) is only valid for operation at a very low current density (*i.e.*, a low current and/or high surface/geometric area at/of the *counter electrode* (CE)), so that any polarization effects at the CE can be neglected.

In contrast, the electrodes in either *two-electrode* or *three-electrode configuration*, which are cell voltage-controlled (*full cell setup*), are named N and P, as introduced above (**Figure 1 (d) and (e)**). In order to control and monitor the electrode potential of the WE, measured in V *vs. reference electrode* (RE), it must be coupled with a *reference electrode* (RE) having a fixed electrode potential.[16] This setup, where simply the potential of the WE is monitored, under open circuit potential (OCP) (= "currentless") conditions is called "*half-cell setup*" (**Figure 1 (z)**). It is the general setup in order to experimentally determine electrode potentials of half-cells, *e.g. via* a standard hydrogen electrode (SHE) RE. In contrast, standard electrode potentials of the electrochemical series, like $Cu|Cu^{2+}$, are derived from *e.g.*, the Nernst equation.

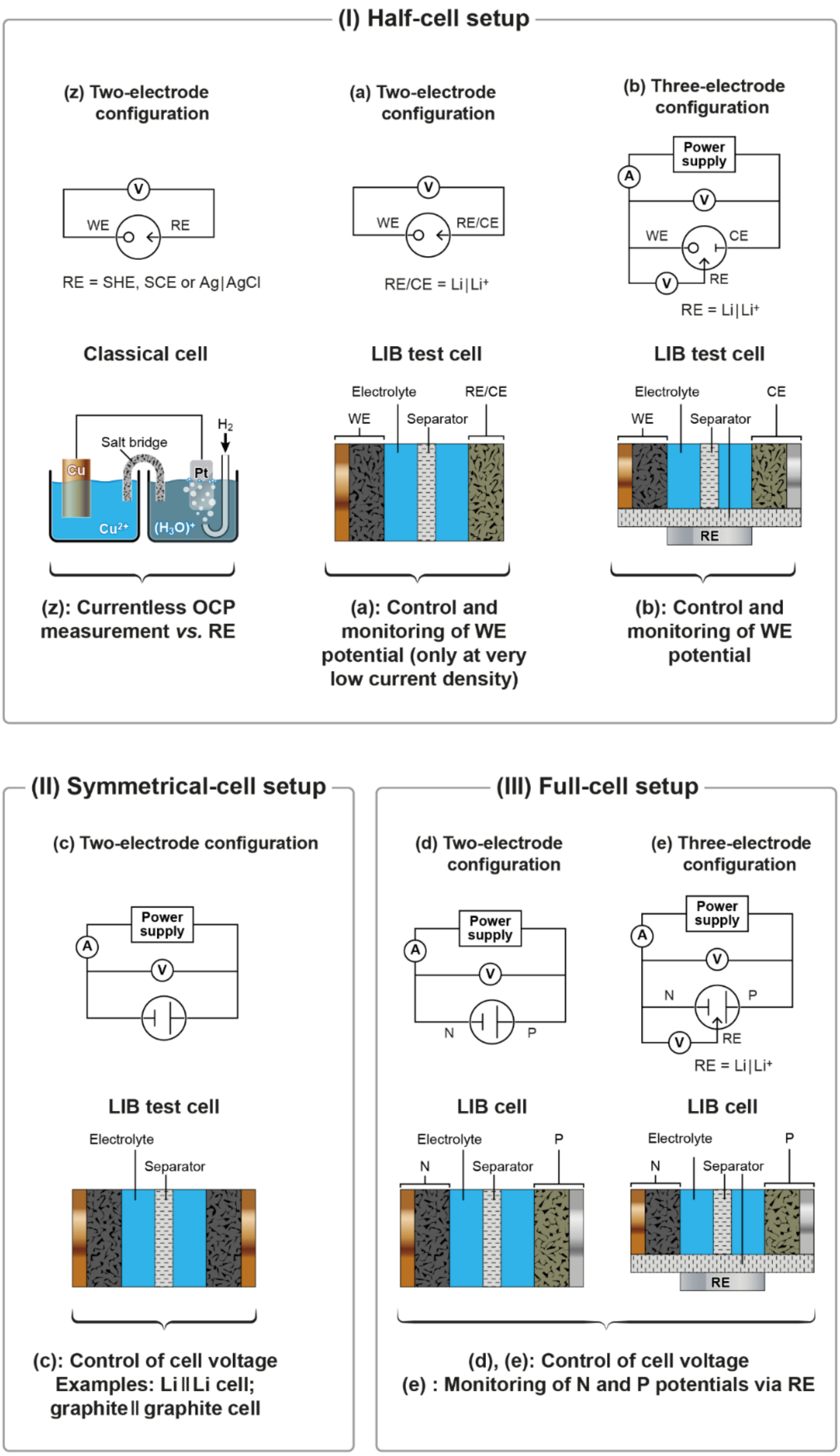

Figure 1: Overview of the different cell setups typically used in battery research. (I) *half-cell setup*, including (z) setup for OCP measurement *vs*. RE (currentless), (a) *two-electrode configuration* (gives only accurate electrode potentials at very low current density at RE/CE) and (b) *three-electrode configuration*; (II, (c)) *symmetrical-cell setup;* (III) *full-cell setup*, including (d) *two-electrode configuration* and (e) *three-electrode configuration*. N: negative electrode, P: positive electrode, WE: working electrode, CE: counter electrode, RE: reference electrode, A: amperemeter, V: voltmeter, SHE: standard hydrogen electrode, SCE: saturated calomel electrode, Ag|AgCl: silver|silver chloride reference electrode, Li|Li$^+$: Li metal/Li$^+$-electrolyte reference electrode.

A good and suitable RE is defined by a high reproducibility, reliability and non-polarizability (currentless operation mode) over prolonged operation.[16,17] The primary reference electrode is the *standard hydrogen electrode* (SHE) or *normal hydrogen electrode* (NHE).[18] Other REs used in literature are the *saturated calomel electrode* (Hg|Hg_2Cl_2, SCE), which has a potential of 0.242 V *vs.* NHE and the *silver|silver chloride electrode* (Ag|AgCl), showing a potential of 0.197 V *vs.* NHE.[16] However, for non-aqueous electrolytes and especially in LIB research it is difficult to implement the aforementioned REs into the cell system. For this reason, Li metal in a Li^+ containing electrolyte (= redox couple: Li|Li^+) is often used as RE in LIB research.[19-21] It is common practice to see these electrode potentials in the literature given as "*vs.* Li|Li^+". Besides Li|Li^+, also other electrodes based on materials exhibiting a flat lithiation/de-lithiation potential, based on a biphasic lithium insertion mechanism, are frequently used as RE, *e.g.* $Li_4Ti_5O_{12}$ (LTO)[17,22,23] or $LiFePO_4$ (LFP)[17]. Prior to their application as RE, LTO and LFP are lithiated and de-lithiated to a state-of-charge (SOC) of ≈50% in order to guarantee a stable and highly reproducible electrode potential over the entire operation of the cell.[17] However, these REs give rise to higher experimental expenditure and are therefore commonly replaced by Li|Li^+ due to simplicity. Due to the lack of thermodynamic equilibrium and the fact, that Li|Li^+ is not an ideal non-polarizable electrode, the Li|Li^+ RE is called *pseudo-reference electrode*.[18,24] Nevertheless, when a Li|Li^+ electrode is just used in order to measure the electrode potential of the WE in a *potentiometric* experiment (I = 0) with the help of a high impedance voltmeter (*i.e.* a voltmeter with an internal resistance, high enough to avoid any appreciable current flow during the measurement), the potential of the Li|Li^+ electrode can be considered as being constant.[16]. Recently, Raccichini *et al*. published a comprehensive review article on the use of REs, highlighting critical aspects for their practical use, such as electrochemical analysis methods, cell geometry, *etc*.[25]

Given the importance to measure the potential between RE and WE during cycling under *currentless* conditions, a third electrode must be utilized in order to donate or accept electrons (and lithium ions in case of a LIB cell), thus creating electron and ionic currents needed for cycling. This electrode is usually called *counter electrode* (CE).[16] A *half-cell setup* in a *three-electrode configuration*, as shown in **Figure 1 (b)**, is obtained by the use of WE, CE and RE. In this setup, the cut-off conditions during charge/discharge cycling are controlled by the WE electrode potential *via* the RE.[18,26]

The use of Li metal as "auxiliary" opposite electrode (CE) to the electrode/material of interest (WE) provides an almost unlimited amount of active Li (=Li^+ + e^-), which is a main advantage for fundamental studies on novel electrodes/materials.[27] However, there are also various drawbacks of this setup, as will be described in the following sections. It is also possible to use a typical LIB electrode, *e.g.* a graphite or LFP electrode, as opposite electrode to the electrode/material of interest. This has the advantage of a more realistic measurement, especially when the cell voltage is used to control the cut-off conditions (*full-cell setup*). Nevertheless, in this setup it still remains possible to monitor the electrode potentials of the N and P electrodes with help of a Li metal RE, independently (**Figure 1 (e)**). This allows a more precise investigation of the influence of the individual electrodes on the ongoing processes, such as SOC development, polarization, dendrite formation or the rate capability of each electrode, inside the LIB cell.[22,28-31] Furthermore, for impedance measurements, geometry and location of the RE is a factor of central importance, but beyond the scope of this review article.[25,32-36]

As discussed above, it should be mentioned that a *two-electrode configuration*, which uses Li metal as N, can only be described as *half-cell setup* at very low current density at the Li metal electrode (**Figure 1 (a)**). However, this notation is not correct at moderate/high current density, due to the fact that the current load leads to a voltage drop (also called "*IR*-drop" + overpotentials) as described in **Equation 1**, in which I is the current, η is sum of all overpotential, R_S the resistance of the electrolyte between the two electrodes and E_{appl} and E_{eq} are the applied and equilibrium potential, respectively.[16]

$$\boldsymbol{E_{appl} = E_{eq} + \eta + I \cdot R_s} \qquad (1)$$

In addition, individuals or companies working on lithium-sulfur (S || Li) and lithium-oxygen (O_2 || Li) two-electrode rechargeable full cells or selling MnO_2 || Li or I_2 || Li two-electrode primary full cells would not describe these cell configurations as "half cells". Furthermore, due to kinetic hindrances, Li metal electrodes can exhibit strong overpotentials during the Li dissolution/deposition processes[37], which are strongly influenced by the applied current density, as shown by the overvoltages for a Li || Li *symmetrical-cell setup* (**Figure 1 (c)**) in *two-electrode configuration* in **Figure 2**. Therefore, the measurement of the cell voltage within a *two-electrode configuration* with Li metal electrode will be distorted compared to the potential measurement of the WE in a *three-electrode configuration* with Li metal CE including a RE, thus, most likely resulting in a misinterpretation of the performance of the electrode of interest in the *two-electrode configuration*.[17] For this reason, we prefer the term "*Li metal cell*" for such a *two-electrode configuration (full-cell setup)*, instead of "*half-cell*" or *half-cell setup*".

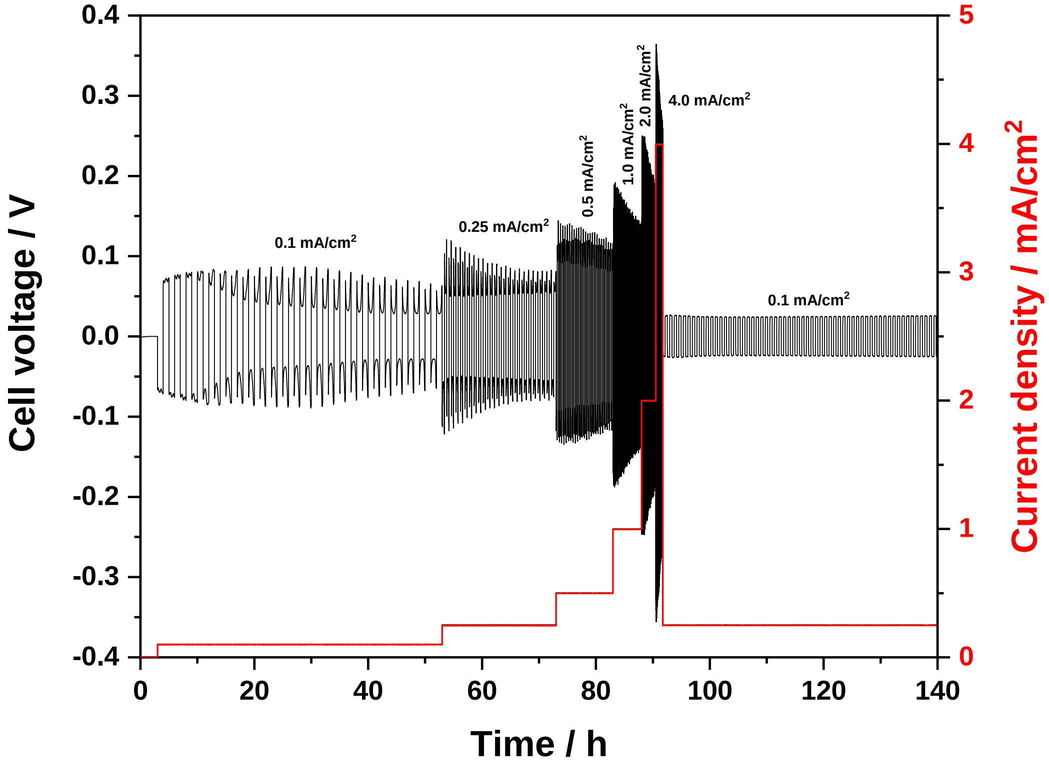

Figure 2: Cell voltage of a symmetrical Li || Li coin cell during continuous Li dissolution/deposition (0.113 mAh) at different current densities at 20 °C.[38] The electrolyte contained 1M lithium hexafluorophosphate ($LiPF_6$) in ethylene carbonate (EC) and ethyl methyl carbonate (EMC) 3:7 (by weight). Dependent on the applied current density, the overvoltages can reach values of more than 300 mV.

Unfortunately, in battery research-related literature, the term "half-cell" is often used for many different setups/configurations, *i.e.* to either describe a *half-cell setup* which is potential-controlled (as defined above, see **Figure 1 (I)**) or to describe *two-* or *three-electrode configurations* which are cell-voltage controlled and use *e.g.* Li metal as negative electrode (N). However, the use of this notation is not favourable and actually also not correct according to textbook electrochemistry knowledge[16], as the latter setup should be correctly named *full-cell setup* (**Figure 1 (III)**). In this respect, also different terms such as "cell voltage", "cell potential" and "electrode potential" are often used in literature. However, these terms are also sometimes mixed up and used incorrectly, *e.g.*, as "electrode voltage". Therefore, we recommend to explicitly use the terms "cell voltage" (in V; difference of the potentials of P and N) and "electrode potential" (in V *vs.* Li|Li^+ (or *vs.* other REs). As a result of the unclear usage of these terms and due to the fact that in various literature reports often insufficient information is given about cell setup, the cell configuration and the way of electrode potential or cell voltage control, it is hard to understand and compare results of different studies.

In turn, in order to achieve a better understanding and better comparability between different material, electrode or cell characterizations it is of utmost importance to establish a proper use of these terms. Therefore, we strongly encourage researchers to use the suggested terms and to give a clear definition in their electrochemical studies about 1) the cell setup (half-cell *vs*. symmetrical-cell *vs*. full-cell), 2) the electrode configuration (two-electrode *vs*. three-electrode) and 3) whether the cell is controlled by the cell voltage or by the WE potential *via* a RE. In case of cell voltage controlled cells, it should also be mentioned if electrode potentials are additionally monitored *via* a RE.

To summarize, we recommend to use the following definitions and terms for the different cell setups and configurations for an unambiguous and clear description of fundamental electrochemical studies of materials and electrodes. A simplified summary and comparison of the different cell setups is shown in **Table 1**.

(a) Electrodes:

- The terms WE, CE and RE are used for *half-cell setups* in *two-electrode configuration* (**Figure 1 (a)**) or *three-electrode configuration* (**Figure 1 (b)**), in which the WE potential (in V) is either measured at very low current density or in which the WE potential (in V *vs*. RE) is controlled and monitored *via* a RE.
- The terms N and P are used for *full-cell setups* in *two-* or *three-electrode configuration* (**Figure 1 (d) and (e)**), in which the cell voltage (in V) is controlled and monitored. Additionally, the electrode potentials (in V vs. RE) of N and P can be monitored *via* a RE (**Figure 1 (e)**).

(b) Cell setups and configurations:

- *Half-cell setup (two-electrode configuration)*: This is a general cell setup in order to determine/monitor the **electrode potentials** of half-cells (**Figure 1 (z)**) under open circuit potential conditions with help of a suitable RE (= "currentless" measurement conditions). Furthermore, it is possible to measure **electrode potentials** in this setup at sufficiently low current density, so that polarization effects at the RE/CE (*e.g.*, Li metal) can be neglected (**Figure 1 (a)**).
- *Half-cell setup (three-electrode configuration)*: The cell is operated by control and monitoring of the **electrode potential** (*vs*. RE) of the WE, *i.e*. by cut-off potential control during constant current charge/discharge measurements and by potential control in constant potential steps or in voltammetric experiments (cyclic voltammetry, linear sweep voltammetry, *etc*.). In turn, the potential of the CE (and the resulting cell voltage) will also

vary in dependence of the used materials and operation conditions and can be monitored *via* the RE (**Figure 1 (b)**). In such cases, account must be taken of the fact that the CE should be designed to not affect the cell performance in any way.

- <u>*Symmetrical-cell setup* (*two-electrode configuration*):</u> The cell is operated by control of the **cell voltage** during charge/discharge (**Figure 1 (c)**). Examples include Li || Li cells or graphite || graphite cells. A special case, in literature also described as symmetric cells, is the coupling of the same electrode material in the lithiated and the de-lithiated state (*i.e.* lithiated graphite || graphite, lithiated LTO || LTO *etc.*).[39-42] However, since these cells are, respective to the mathematical definition of symmetry, not symmetrical after assembly, we would prefer the term "*pseudo symmetrical cell*" for such types of cell setup.
- <u>*Full-cell setup* (*two-electrode configuration*):</u> The cell is operated by control of the **cell voltage** during charge/discharge. The potentials of N and P will vary simultaneously in dependence of the used materials and operation conditions (**Figure 1 (d)**). A special case is the combination of a Li metal electrode (N) and an electrode of interest (P). This setup should not be described as "*half-cell setup"*, but the term "*Li metal cell*" is suggested instead. This is due to the fact that the current load leads to a voltage drop (= IR drop and overpotentials at N), which will influence the measured cell voltage and, thus, might lead to a misinterpretation of the performance of the electrode of interest.
- <u>*Full-cell setup* (*three-electrode configuration*):</u> The cell is operated by control of the **cell voltage** (cut-off voltages) during constant current charge/discharge cycling. The potentials of N and P will vary in dependence of the used materials and operation conditions, but can be monitored simultaneously *via* a RE (*e.g.* $Li|Li^+$) (**Figure 1 (e)**).

Table 1: Comparison of different cell setups typically used in battery research, in analogy to **Figure 1**. *: An accurate measurement of electrode potentials is only valid at very low current density at the RE/CE.

	*Half-cell setu*p **(a)**; *2-electrode configuration*	*Half-cell setup* **(b)**; *3-electrode configuration*	*Symmetrical-cell setup* **(c)**; *2-electrode configuration*	*Full-cell setup* **(d)**; *2-electrode configuration*	*Full-cell setup* **(e)**; *3-electrode configuration*
Nomenclature of electrodes	WE, RE/CE	WE, CE, RE	---	P, N	P, N, RE
Electrochemical operation conditions	Control of cell voltage (≈WE potential*)	Control of WE potential	Control of cell voltage	Control of cell voltage	Control of cell voltage
Monitoring of single electrode potentials	Yes*	Yes (*via* RE)	No	No	Yes (*via* RE)
Graphical illustration in	Figure 1 (a)	Figure 1 (b)	Figure 1 (c)	Figure 1 (d)	Figure 1 (e)

Special cases are, when a constant voltage step or constant potential is applied, for instance, at the end of the charge or discharge process[43,44] or when the linear scanning voltammetry or cyclic voltammetry techniques are applied. In these cases, there is not only a cut-off voltage/potential control but also a general voltage/potential control during the course of the experiment (step). Within this review, we want to focus on the different applications of the above introduced cell setups and configurations and evaluate their correspondent advantages and disadvantages, especially with focus on the use of Li metal as CE. The aim of this work is to highlight the major mistakes and misinterpretations that can occur by using different cell setups and to provide the reader a recommendation about reasonable fields of application for a specific cell setup/configuration.

3. Challenges for the electrochemical study of active materials and electrolytes for LIBs: A guide to choose the appropriate cell setup and configuration for academic researchers

3.1 Study of positive electrode materials for LIBs

3.1.1 Relevance of precise electrode potentials for positive electrode research

State-of-the-art (SOTA) positive electrode materials for LIBs are “layered transition metal oxides” based on Li*TM*O_2 (*TM*= Co, Ni, Mn, Al, *etc*.) stoichiometry, *e.g.* $LiCoO_2$ (LCO) or $LiNi_xMn_yCo_zO_2$ (NMC, with x+y+z=1).[45-47] Their solid-solution type delithiation/lithiation mechanism implies a distinct dependency of the positive electrode potential on the delithiation/lithiation amount (specific charge/discharge capacity), thus, from the SOC of the LIB cell.[12,48] The relation of specific capacity and positive electrode potentials is exemplarily shown for the $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC111) potential curve in **Figure 3**.[43] Increasing the delithiation amount (or Li^+ extraction ratio) *via* increase of the charge cut-off potential of the positive electrode, leads to an increase of the specific energy (specific capacity and cell voltage), but typically at the expense of stability and safety.[49,50] Exceeding a threshold delithiation amount results in thermodynamically driven structural changes, leading to decreased cycle life and increased safety issues (*e.g.* O_2 evolution from LCO when exceeding 50% Li^+ extraction).[51-53] Consequently, for a given specific current, the charge cut-off potential dictates the Li^+ extraction ratio and the related performance/safety aspects and finally must be precisely controlled for positive electrode research.[54]

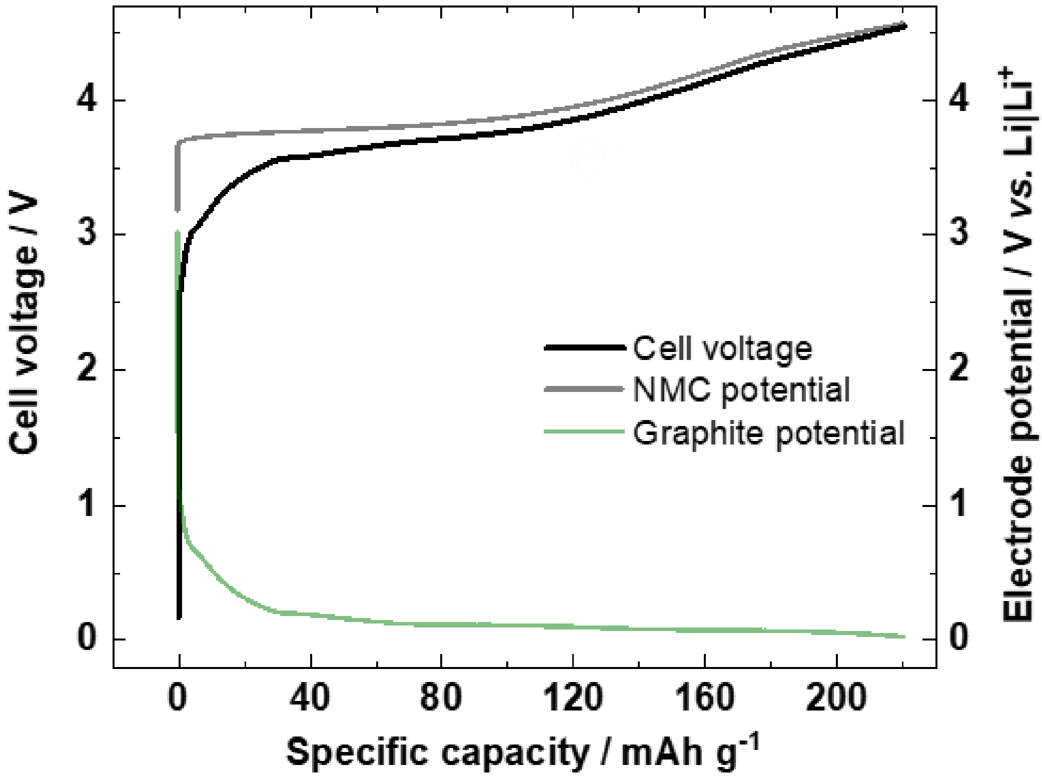

Figure 3: Dependence of electrode potentials and cell voltage *vs.* specific capacity in a $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC111) || graphite *full-cell setup* (*three-electrode configuration*) during charge at the cell cut-off voltage of 4.55V (corresponds to NMC111 and graphite potentials of 4.60 and 0.05 V *vs.* Li|Li^+, respectively). Electrode potentials are monitored using a Li metal RE. Redrawn from ref.[43]

3.1.2 Challenges of a full-cell setup related to undesired shifts in electrode potentials

The investigation of battery materials (*e.g.* positive electrode materials) in dependence of a precise electrode cut-off potential can reasonably only be realized *via* the use of a RE. As in a *full-cell setup* with *two-electrode configuration* only the cell voltage can be controlled and monitored (no RE), the electrode potentials cannot be directly targeted. The relation of the cell voltage and corresponding electrode potentials in a LIB are exemplarily shown in **Figure 3** for a NMC111 || graphite full-cell with the use of a RE. Though, in an ideal case, the electrode potentials can be indirectly adjusted by precise selecting of both, the cell cut-off voltage and balancing of negative electrode (N)/positive electrode (P) capacities (N/P ratio) - at least for the first charge/discharge cycle.[44] However, minor balancing inaccuracies and/or undesired (electro-) chemical processes within the *full-cell setup* (*e.g.* consumption of active Li^+ due to parasitic reactions in cells without *excess capacity Li metal electrodes*) can lead to undesired shifts of the electrode potentials.[13] The effect of N/P capacity balancing inaccuracies on the electrode potentials already in the first charge step is schematically shown in **Figure 4**. For specific examples of different N/P ratios and the related influence on the shift of the individual electrode potentials, the reader is referred to ref [44].

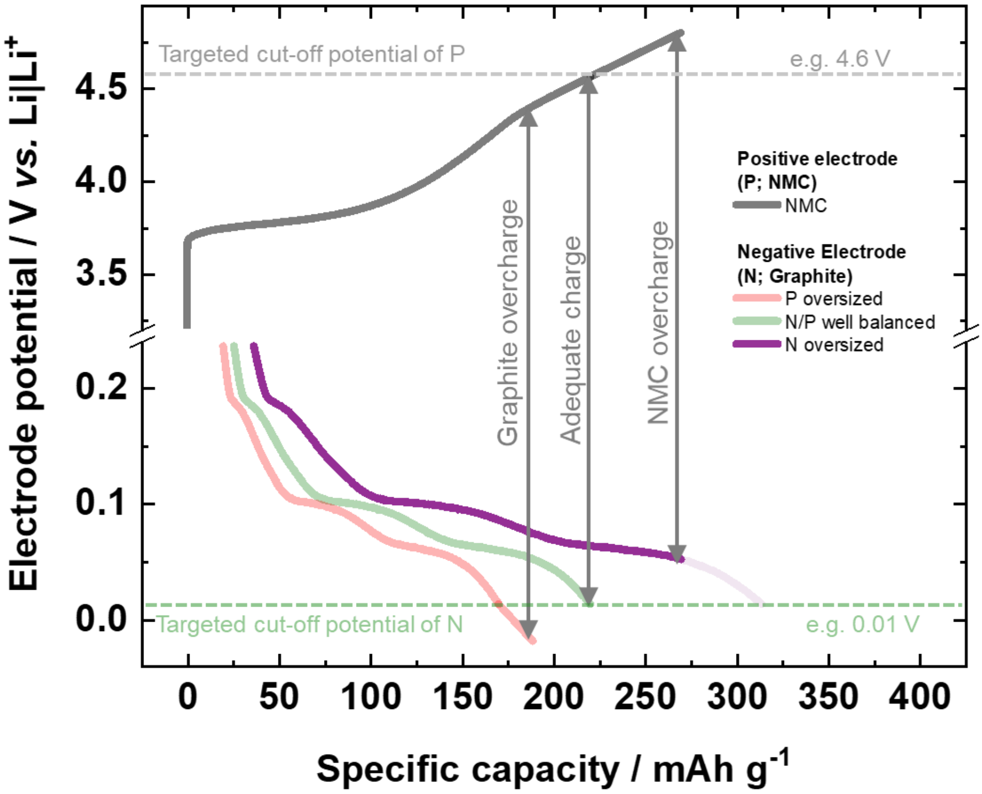

Figure 4: Schematic illustration of the N/P balancing influence on the electrode potentials in a NMC || graphite LIB full-cell. Oversizing of the positive electrode (P) or negative electrode (N) can lead to a shift in electrode potentials (for a charge cut-off voltage set constant) up or down, resulting in overcharge of P or N, respectively. The length of the arrow corresponds to the potential difference of P and N (=cell voltage). Redrawn from ref.[44]

In an ideally balanced *full-cell setup*, the selected charge cut-off cell voltage would target the intended electrode potentials (green potential curve of N, **Figure 4**). In the case of a (mistakenly) capacity-oversized P, the electrode potentials for both electrodes would decrease for the set cut-off cell voltage, resulting in overcharge of N (red potential curve of N), which in turn would result in capacity loss and safety issues due to unwanted Li metal plating at N. In the opposite case (when N is oversized, *i.e.* > ≈10-15%), the electrode potentials for both electrodes would increase at the set charge cut-off cell voltage, resulting in overcharge of P (violet potential curve of N). In practice, such quality of N/P balancing can be indicated by the obtained initial specific charge capacity (too low or too high specific charge capacity would indicate oversizing of P or N, respectively).[44] As pointed out by this example, the (initially) targeted electrode potentials under cell voltage cut-off control in a *full-cell setup* are sensitively volatile, which gets stepwise more severe during subsequent ongoing charge/discharge cycling. As shown in **Figures 3** and **Figure 4**, the electrode potentials can be indirectly targeted within a *full-cell setup via* accurate cell voltage adjustment, at least in theory. In practice, overpotentials may evolve during ongoing charge/discharge cycling of N and/or P, which can significantly shift the electrode potentials compared to the ideal case, where scenario (a) represents the ideal case (**Figure 5**). When the overpotential evolves at P, the shift can occur to higher potentials for both electrodes, as seen in **Figure 5** (scenario (b)). When the overpotential evolves at N, the shift can occur to lower potentials for both electrodes, as seen in **Figure 5** (scenario (c)). When overpotentials evolve at both electrodes, a shift can occur in dependence of which overpotential (N *vs.* P) is higher, as seen in **Figure 5** (scenario (d)). Each overpotential scenario would lead to a decreased specific capacity, thus, Li^+ extraction ratio of P. Particularly for positive electrode research, evolving overpotentials of N (scenario (c) or (d)) and a related shift to lower potential values at both electrodes would significantly affect the positive electrode chemistry/performance by decreasing the Li^+ extraction ratio. Often, misinterpretations occur, when positive electrode materials are only investigated without a RE (*i.e.* in a *two-electrode configuration*). For example, when investigating electrolytes, which simply raise the overpotential of N (scenario (c), **Figure 5**), *e.g.* due solid electrolyte interphase (SEI) and corresponding impedance formation, P would have a lower Li^+ extraction ratio, but be structurally more stable and performing better in terms of cycle life and safety. Therefore, it would be incorrect to attribute the apparently better stability of P to a positive electrolyte at the cathode, as in fact there is no direct causal correlation. This effect is especially pronounced for positive electrodes exhibiting two-phase reaction mechanisms, where the electrode potentials remain relatively stable over a wide range of the SOC (*cf.* LFP, LNMO) and where a small change in the electrode potential can have a severe impact on capacity. Those misinterpretations can be prevented by the use of a RE, where the individual electrode potentials of P and N can be monitored during cell voltage-controlled operation and, therefore, possible overpotentials evolving at P and/or N can be identified.

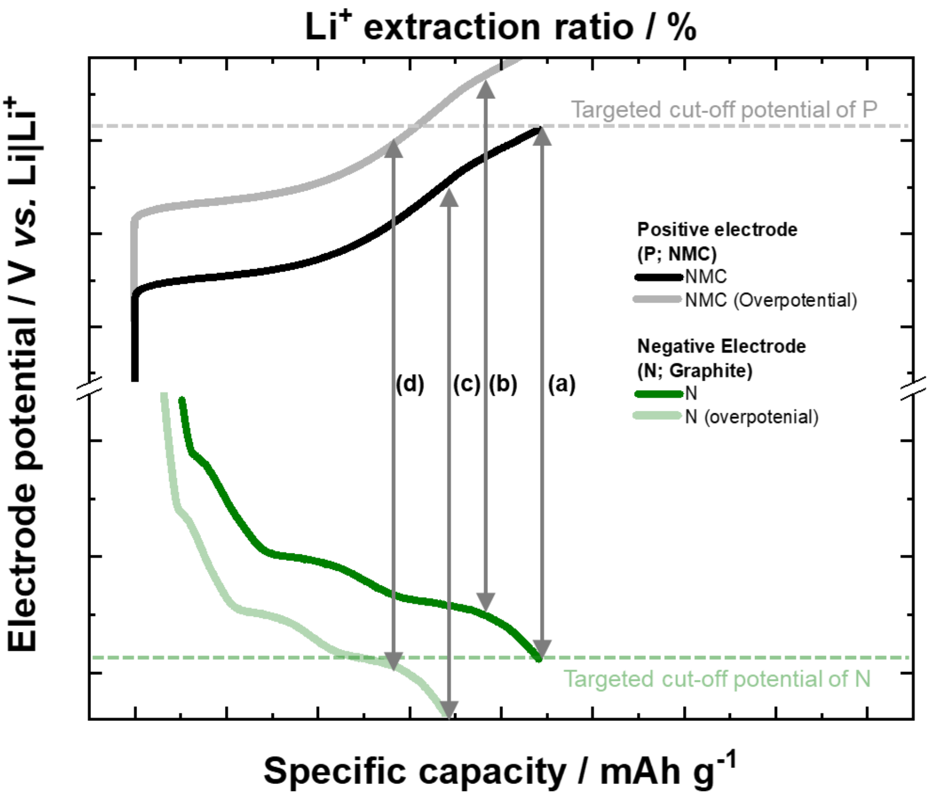

Figure 5: Schematic illustration of possible influences of overpotentials at P (=NMC111) and/or N (=graphite) on the shift in electrode potentials and specific capacity in a NMC111 || graphite LIB *full-cell setup* for a constant charge cut-off voltage. In the absence of overpotentials, the electrode potentials can be targeted indirectly by the charge cut-off cell voltage, as shown for scenario (a). When an overpotential would evolve at P (b), both electrode potentials would shift up (electrode potentials at cut-off voltage are higher for (b) compared to (a)). When an overpotential would evolve at N (c), both electrode potentials would shift down (electrode potentials at cut-off voltage are lower for (c) compared to (a)). In case overpotentials evolve at both electrodes (d), a shift would occur in dependence of which overpotential is higher (compared to (a)). In all cases (c-d), the overpotentials would lead to a decay in specific capacity, thus, to a decrease of Li^+ extraction ratio of P, which is a significant parameter for the electrochemical performance of P (specific energy *vs*. cycle life).

3.1.3 Challenges for a full-cell setup related to loss of active Li (negative electrode with no active Li excess, e.g. graphite)

Positive electrode materials are the source of active Li (Li^+ + e^-) in conventional LIBs, thus, the source of specific cell capacity. For a reasonable investigation of performance related characteristics, particularly the investigation of the specific capacity of single positive electrodes, the negative electrode should not irreversibly "consume" active Li. However in practice, graphite as SOTA negative electrode consumes a significant amount of active Li[19], which is required for the solid electrolyte interphase (SEI) formation in the first charge/discharge cycle(s), *e.g.* when using graphite-based negative electrodes.[55-57] As the amount of active Li is limited by P in those *full-cell setups*, the consumption of active Li by N results automatically in less specific capacity for P as well as less specific cell capacity. This relation is exemplarily shown in **Figure 6** for a NMC111 || graphite *full-cell setup*. In this example, the consumption of active Li by graphite leads to high specific capacity loss of N, which means that less active Li is released during discharge than accepted during previous charge. The completed release of remaining reversible active Li (seen by the almost vertical potential slope of N) leads to the termination of the discharge process, as a certain cut-off cell voltage is reached. This has a significant effect on the characteristics of P. The released active Li of P during charge is not fully recovered during subsequent discharge due to the losses of active Li at N. Though the full-cell is in the discharged state, P is still not completely discharged (=lithiated), as the single positive electrode could theoretically accept more active Li as implied by the dotted line in **Figure 6**, which would be observed when measured in a *cell setup* with Li-excess N (*Li metal cell*) or a Li-excess CE (*half-cell* in *three-electrode configuration*). Moreover, in a conventional NMC111 || graphite *full-cell setup*, active Li losses can accumulate during continuous charge/discharge cycling. This can additionally leads to the shift of the electrode potentials to higher values at a charge cut-off cell voltage, as described in **Figure 5** (scenario (b)), finally inducing undesired overcharge of P, as previously also described in ref.[13] Note, that the capacity loss/irreversible capacity of positive electrodes may be only of kinetic nature.[43,49,53]

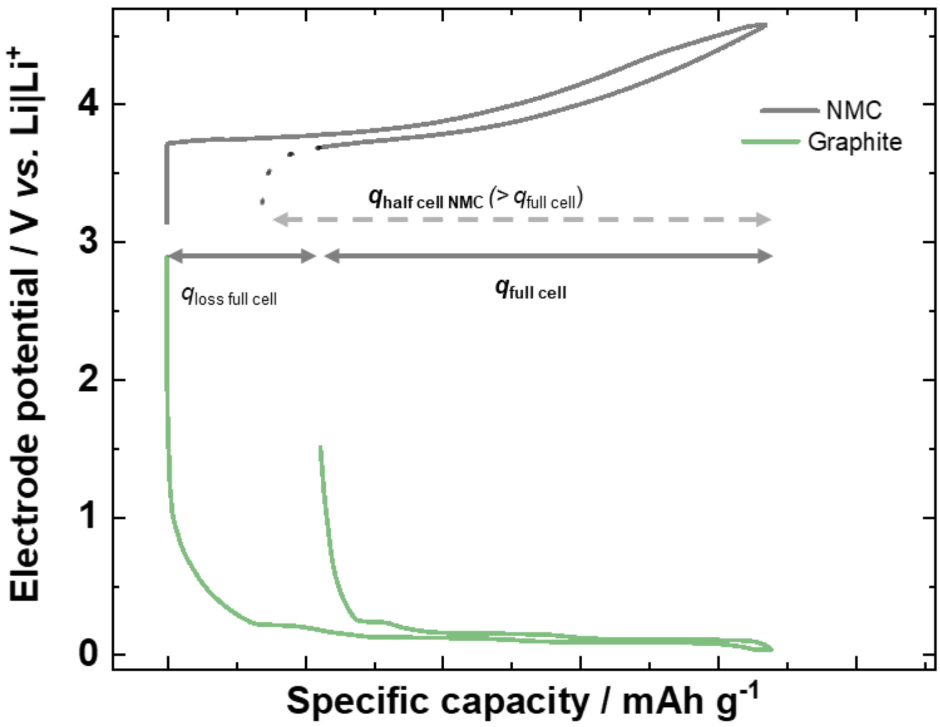

Figure 6: Electrode potential curves of a NMC || graphite LIB *full-cell setup* for P (=NMC111) and N (=graphite). High amounts of active Li loss at N can lead to an incomplete lithiation/discharge of P in a *full-cell setup* with graphite N, thus, to lower specific capacities compared to the performance of P in a cell setup with Li metal N or CE, which is indicated with a dotted line.

It can be concluded that a *full-cell setup* (*three-electrode configuration*) using an N electrode with active Li excess (*Li metal cell*) provides information on P electrodes, that cannot be obtained with a graphite N electrode, *i.e.*, the determination of the reversible capacity of P by excluding an influence of an active Li consuming N. Though, Li metal can also be used in a *full-cell setup* in *two-electrode configuration* as N (*Li metal cell*), the investigation of P would still be inaccurate, since the presence in current flow leads to overpotentials and formation of high surface area lithium (HSAL), thus, to additional overpotentials (*cf.* section 2 and **Figure 2**).[37,55] The performance of P would be significantly affected as schematically described for scenario (c) in **Figure 5**. When using a RE in a *half-cell setup*, the kinetics/overpotentials of the CE would not affect the kinetics/overpotentials of the WE, as demonstrated for a modified (varied CEs) *half-cell setup* in ref.[58]. A possibility to achieve reliable results also in *two-electrode configuration* using a Li metal N is the application of a constant current-constant voltage (CCCV) cycling procedure, *i.e.* by applying an additional constant voltage step at the set cut-off voltage until the current drops below a defined (very small) value. Since the IR drop and/or overpotentials are dependent on the current density, as already discussed in the previous sections, overpotentials at the Li metal N will become negligibly small during the constant voltage step to allow for achieving the intended cut-off potential of P (*i.e.* cell voltage ≈ electrode potential). However, it has to be kept in mind that during the constant current step, the controlled and monitored cell voltage cannot be equalized to the electrode potential of P, as the overpotential evolving at the Li metal N during plating/stripping shifts the cell voltage to higher/lower values, respectively.

In summary, fundamental investigations for screening of positive electrode materials should proceed in a *half-cell setup* in *three-electrode configuration* with a Li excessed CE for reasons of accurate capacity and WE potential measurements. At least measures like using a CCCV protocol need to be undertaken, when using a Li metal N within a *two-electrode configuration* (Li metal cell) for investigation of P materials. Nevertheless, investigation of positive electrode materials in combination with electrolyte formulations can be challenging, as some electrolytes (*e.g.* some aliphatic nitriles[59]) are not compatible with Li metal, thus, rendering a measurement *via* a *half-cell setup*, containing a Li metal CE and/or RE, impossible.[60] In addition, a *half-cell setup* does not entirely represent the complexity within a LIB full-cell, *e.g.* electrolytic crosstalk with N, particularly when it comes to investigations of electrolyte additives, which will be emphasized in the subsequent section. In this respect, we recently reported on the "cross-talk" between different transition metal-based P and a Li metal N in *Li metal cells,* showing that transition metal dissolution from P has a severe impact on the plating/stripping behavior, SEI formation and overpotential on the Li metal N.[61] In turn, a simple comparison of different positive electrode materials in *Li metal cells* will have further challenges and might not be sufficiently accurate. Therefore, when it comes to an assessment of the practicality of positive electrode materials (*e.g.*, long-term charge/discharge cycling studies), we recommend to perform studies in a *full-cell setup* (*two- or three-electrode configuration*) without active Li excess negative electrodes. Thereby, monitoring of the single electrode potentials in a *three-electrode configuration* will help to understand mechanisms of capacity fading and aging.

3.2 Study of electrolyte formulations and electrolyte additives for LIBs

3.2.1 Introduction to electrolytes and additives

SOTA electrolyte systems for LIBs are both chemically and electrochemically metastable and, thus, they are susceptible to irreversible decomposition close to the electrode/electrolyte interfaces, affecting the overall cell performance and often triggered by overcharge or overdischarge beyond the limiting electrochemical stability potential windows, elevated operating temperature and trace moisture.[62,63] By adding small amounts of other components into the electrolyte system, it is possible to tailor specific targeted properties of the electrolyte without changing the bulk properties.[45,64] *Kang Xu* defined an electrolyte component of less than 10% as electrolyte additive.[65] Besides the development of advanced active materials, the use of suitable electrolyte additives seems to be one of the most beneficial, economical and effective solutions to improve overall LIB performance, thus, constituting an important research and technology field.[66] Various literature reports deal with the influence of electrolyte additives either in *half-cell* and/or *full-cell setups* in *two-* and/or *three-electrode configurations*.[66] This section summarizes the repercussions of applying a *two-* or *three-electrode configuration* for electrolyte additive investigations and clearly works out possible limitations and error sources depending on the underlying scientific questions.

3.2.2 Pros and Cons for electrolyte additive investigation in different cell setups and configurations

Today, a great number of electrochemical measurement techniques to investigate electrolyte systems are reported in literature, enabling access to a variety of electrolyte additive-related scientific questions and challenges.[39,62,65-67] These include *e.g.* a) the kinetic electrochemical stability of the electrolyte and impact of additives thereon, b) the effect of electrolyte additives on charge/discharge cycling performance, in particular reversible capacity and capacity retention, c) influence of electrolyte additives on SEI and cathode electrolyte interphase (CEI[68,69]) formation at N and P, and d) the influence of electrolyte additives on the development of the respective electrode potentials.[62,65,66]

The commonly used electrochemical measurement techniques for electrolyte additive investigations refer to cyclic and linear sweep voltammetry as well as galvanostatic (=constant current) charge/discharge cycling experiments, formally called as galvanostatic chronopotentiometry. The following discussion places special emphasis on galvanostatic charge/discharge cycling experiments in *half-* and *full-cell setups* and summarizes the operational conditions and limitations of each cell system applied in a *two-* and *three-electrode configuration*.

Many research studies on electrolyte additives in combination with different LIB active materials show cycling results obtained in a *full-cell setup* (*two-electrode configuration*) using metallic Li as N.[70,71] In such a setup, also classical N active materials (according to their designation in a LIB *full-cell setup*) are always considered as P, *e.g.* when silicon/carbon composite (Si/C) materials (here: P) are studied *vs*. Li metal (N). As explained for **equation 1** and according to the above discussions, the resulting cell voltage does not allow any direct conclusion on the respective electrode potential of the electrode of interest (this would only be possible at sufficiently low current densities, as discussed in previous sections). Furthermore, possible overpotentials, generated or diminished by a certain electrolyte component during the dissolution and deposition process of Li on the Li metal N [72-75], influence the development of the potential of the electrode of interest and might cause misinterpretations due to potential dependent lithiation and/or de-lithiation degrees as schematically shown for scenario (c) in **Figure 5**. Therefore, it is not possible to differentiate whether the positive effect of this electrolyte additive is due to a beneficial interphase (SEI or CEI) formation on/at the active material (at P) or simply on/at the Li metal N.[69] Therefore, we cannot recommend to use such a setup for electrolyte solvent/salt/additive studies.

With help of a *half-cell setup* (*three-electrode configuration*) including a suitable RE, it is possible to cycle the WE with help of the RE to a precise cut-off potential and, thus, to exclude any error source arising from the Li metal CE. However, it is also important, but unfortunately often disregarded that the precise control of charge/discharge cycling to a certain cut-off potential in a *half-cell setup* may provoke the formation of unique interphases that may differ in composition and thickness compared to the interphases formed in a *full-cell setup*.[55,76] For example, Vogl *et al.* showed that the SEI formation and the resulting composition on a single crystal Si(100) electrode strongly depends on the electrode potential.[77] Furthermore, Nie *et al.* observed a gradual increase of the SEI thickness on graphite, as the cell was cycled to lower potentials.[78] As an example, a lower cut-off potential of 20 mV *vs.* $Li|Li^+$ or less is often applied in graphite || Li metal *half-cell setup* experiments with $Li|Li^+$ RE. By using a N/P-ratio >1 (capacity-oversized negative electrode to avoid Li plating[13,44]) in a *full-cell setup*, these low potentials of N are typically not reached and, thus, a potential dependent impact on the composition and thickness of the formed SEI layer cannot be excluded. Furthermore, due to its highly reducing ability, an increased amount of electrolyte is irreversibly consumed when Li metal is used as CE and RE, which also may affect the cycling performance, especially when focusing on reactive electrolyte additives with limited amounts in the electrolyte (*cf.* section 3.1.3).[79] In addition, continuous electrolyte decomposition of electrolyte on Li metal will accumulate electrolyte decomposition products in the electrolyte and, thus, in turn may contaminate/alter SEI and CEI, which consist of electrolyte decomposition products.

Numerous publications report on electrolyte additive investigations showing a beneficial effect of the additive on the positive and negative electrode in *Li metal cells*, respectively, without evaluating the performance of the respective additive in the final, targeted LIB *full-cell* *setup*.[70,71] However, the above discussions clearly indicate, that a direct transfer of the results obtained in these Li metal cell setups to a LIB *full-cell setup* may not always be valid. In addition, the choice of N can have an impact on CEI composition at the positive electrode.[79-82] The process involving electrolyte decomposition products, formed at the electrode/electrolyte interfaces, tending to diffuse/migrate through the electrolyte to the opposite electrode, is often defined as "cross-talk" between N and P.[13,81-86] These decomposition products can be involved in the interphase formation on the respective opposite electrodes and can have a significant impact on the desired functionality of a certain electrolyte additive. As introduced above, we recently reported a study on the "cross-talk" of different transition metal-based P and a Li metal N in *Li metal cells,* showing the severe impact of transition metals dissolved from P on the plating/stripping behavior and SEI formation on the Li metal N.[61] As a consequence, to obtain reliable and representative results for the performance of electrolyte/additives and for the composition, structure and thickness of interphases (SEI, CEI), the study in a LIB *full-cell setup* measurement without Li metal electrodes is highly recommended.

Taken these effects into consideration, a more feasible way to screen a large number of electrolyte additives is applied in the manufacturing of full-cells with the active materials of interest in a *two-electrode configuration*. Due to the considerable need for highly reproducible cells, which basically differ in the electrolyte additive, machine-made electrodes and cells produced by battery manufacturers are highly recommended, *e.g.*, as often reported by Dahn *et al*.[87-93] If cells are prepared by hand, researcher should also follow certain guidelines to achieve high quality and highly reproducible cells.[94-97] However, one drawback in the full cell setup without RE is the missing ability to monitor and control the individual electrode potentials, with the disadvantages discussed in chapter 3.1.

Once a suitable additive is found in the LIB *full-cell setup* in *two-electrode configuration,* it is possible to further clarify the working mechanism in a LIB *full-cell setup* in *three-electrode configuration*, identifying the development of each electrode potential independently from each other in order to avoid misinterpretations. The LIB *full-cell setup* (*three-electrode configuration*) allows the monitoring and identification of regular reduction and oxidation processes, overcharge and overdischarge processes, including Li metal plating at N as well as related overpotentials.[50,58,84,98]

There are also attempts to avoid a possible reaction of a proposed electrolyte additive during cycling by changing the N electrode of the *full-cell setup*. The application of LTO-based negative electrodes for studies on CEI forming additives to avoid/diminish a reduction of the additive at N or the use of capacity-oversized LFP positive electrodes (*cf.* section 3.3.2) as less reactive Li source for SEI forming additive investigations is commonly known in literature.[19,82,99-101] Furthermore, to investigate the compatibility of an electrode material of interest with an electrolyte system of choice, *symmetrical-cell setups* are a powerful tool to overcome the issue of cross-talk phenomena between both electrodes. In symmetrical cells, the same material/electrode is used on both sides[102-106], whereby in "*pseudo symmetrical cells"* one of the electrodes is used in the lithiated state and the other one in the de-lithiated state.[39-42] In view of practicality, these cell setups do not allow a transfer to other cell systems, but serve merely for a mechanistic study of the electrolyte additive.

The need for a precise tuning of the electrolyte amount in the respective cell setup is all in common, independent of the cell setup, in order to provide a reliable statement on the required amount of additive in practical, electrolyte-limited LIB cells. However, analytical studies of the formed decomposition products[107] as well as transition metal dissolution (*e.g.* Mn^{2+})[108,109] investigations often require an increased amount of electrolyte in the respective cell setup, which has an enormous influence on long-term cycling behavior as well as on gas formation.[26,86,98,109-116]

In summary, the investigation of electrolyte systems including electrolyte additives places special requirements on the electrochemical cell setup and is strongly related to the addressed scientific question. Therefore, for a precise and comprehensive study on the practicality of electrolytes for LIB cells, we recommend to use a LIB *full-cell setup* (*two-electrode configuration*), most preferably machine-made electrodes for the screening process. The results obtained for a promising electrolyte additive should be further compared to an electrolyte mixture with SOTA additives or additive blends known from literature in order to ensure comparability. Finally, we recommend that the working mechanism of suitable additives should be comprehensively studied in a LIB *full-cell setup* (*three-electrode configuration*) or in a *symmetrical-cell setup*. However, the use of *Li metal cells* (independent from the cell setup or configuration) is not recommended to study electrolytes/additives, which are intended to be used in LIBs.

3.3 Study of negative electrode materials for LIBs with special focus on "alloying"-type materials

3.3.1 Electrochemical studies in cell setups with "auxiliary" Li metal electrode (i.e., excess of active Li)

The most common strategy used in literature to study materials for the negative electrode of a LIB, is the fabrication of a *full-cell setup* (*two-electrode configuration*) containing a Li metal

N, *i.e.*, a *Li metal cell*. Thus, the material/electrode of interest is defined as P in this setup for the following discussion, even though "classical" negative electrode materials are in the focus of study. This cell is then operated/investigated with a constant current charging/discharging procedure within a defined voltage range, *i.e.* a lower cut-off voltage slightly >0 V for lithiation of P and a upper cut-off voltage of typically 1-3 V (dependent on the investigated material; higher voltages are usually applied for so-called conversion materials[117-119]) for de-lithiation of P.[120-123] This quite simple and effective procedure can provide information about the cycling performance of P for a desired number of charge/discharge cycles. As these cells contain a huge excess of active Li provided by the Li metal N, a possible capacity fading can be related to material and/or electrode-intrinsic degradation mechanisms of P, *i.e.* changes in crystal structure (amorphization), particle cracking and disconnection of the active material, binder failure or impedance rise related to SEI growth.[28,124]

There are several issues/limitations, which need to be considered when Li metal is used as N and even more when it is used in a *two-electrode configuration*. Firstly, as already discussed in the previous sections, Li metal is not an ideal N due to its polarizability, *i.e.* showing high overpotentials of up to hundreds of millivolts during dissolution/deposition, depending on the applied current (see **Figure 2**).[17,37,125] Therefore, it is not possible to determine the exact potential of P at the applied cut-off voltages within this setup (only possible when applying very low current densities or an appropriate CCCV cycling procedure). This is a severe handicap, because the lithiation degree of P is determined by the electrode potential and *vice versa* (similar to classical LIB positive electrode materials). Especially for materials like graphite or silicon, which exhibit a two-phase region during lithiation (indicated by a potential plateau, see *e.g.* **Figure 3** for graphite), small differences in the actual P potential can have a huge influence on the lithiation degree and, therefore, the charge capacity of P at the applied cell cut-off voltage. Hence, as already pointed out for "classical" P electrode materials in section 3.1.2, the application of a RE in a *half-cell setup* (*three-electrode configuration*) with Li CE is a more viable method to investigate the material of interest (WE), especially in terms of lithiation/de-lithiation capacity, since the WE can be cycled in a defined cut-off potential range. Secondly, the ascribed dissolution/deposition behavior of a Li metal N causes the formation of HSAL, associated with continuous electrolyte reduction at the fresh Li metal surfaces (*cf.* section 3.1.3).[55,126,127] This leads to a severe consumption/decomposition of the electrolyte, which can deteriorate the performance of the investigated cell and, therefore, making it hard to distinguish the predominant aging origins of the cell related to the Li metal electrode (*i.e.*, N in a *Li metal cell* or CE in a *half-cell setup* in *three-electrode configuration*) or the investigated P.

Furthermore, the Li metal N or CE also serves as active Li reservoir, since typically quite thick (up to 500 µm) Li discs are applied in such cells.[28,124] As already mentioned, the excess of active Li can help to investigate material and/or electrode-intrinsic degradation mechanisms, however active Li consuming parasitic reactions, *i.e.* SEI formation, irreversible Li trapping *etc*. occurring in regular LIB anode materials, are neglected in these investigations, whereas it was shown that such parasitic reactions can be severe, especially for alloying-type negative electrode materials like silicon.[28,124,128]

3.3.2 Electrochemical studies in cell setups excluding the influence of an "auxiliary" Li metal electrode

In literature, three main approaches were implemented to overcome the issues of using a Li metal N (*half-cell setup* and *Li metal cell, two-electrode configuration)* or CE (*half-cell setup, three-electrode configuration*). One option is the investigation of the negative LIB electrode material within a *symmetrical-cell setup*, more precisely in *pseudo symmetrical cells* (*cf*. section 3.2.2). In *pseudo symmetrical cells* using LIB electrode materials, there is a defined amount of active Li available, determined by the amount of the lithiated electrode. Therefore, Li-consuming parasitic reactions, which occur during operation, will show up in a capacity fading of the *pseudo symmetrical cells*. Furthermore, performance characteristics like capacity retention, Coulombic efficiency, the development of overpotentials and related energy efficiencies can be directly correlated to the investigated active material.

Recently, some publications reported the use of a capacity-oversized LFP electrode as P for the investigation of negative electrode materials, especially for silicon-based materials.[19,129-133] These kind of cells sometimes are also called pseudo full-cells, since in a "practical" *full-cell setup* N exhibits a 10-15% oversized capacity compared to P to prevent safety issues related to Li metal plating.[44] Such pseudo full-cells can be utilized as a diagnostic tool to study the performance of N materials within cell setups in *two-electrode configuration* and/or *three-electrode configuration*. By oversizing the capacity of LFP, one can implement a defined Li reservoir to exclude capacity fading related to the depletion of active Li. Furthermore, by the absence of a Li metal N or CE, the issues of HSAL formation and a possible continuous reductive decomposition and consumption of the electrolyte on the Li metal N or CE can be prevented. Furthermore, as already described in section 2, LFP exhibits a very flat lithiation/de-lithiation potential and, therefore, does not only serve as P to provide Li ions, but simultaneously can be used to monitor the potential of the investigated N during cell voltage controlled operation within a *two-electrode configuration*.

The third option to investigate the performance of N (=electrode of interest) without an "auxiliary" Li metal electrode, is the utilization of a LIB *full-cell setup* (in either *two-* or *three-electrode configuration*). Therefore, the negative electrode is coupled with a P material for LIBs, such as NMC. This setup should be applied when N shows a promising performance in the aforementioned setups. Within LIB full-cells the amount of active Li is determined by P and, therefore, Li consuming parasitic reactions, like in *pseudo symmetrical cells*, will lead to capacity loss of the full-cells. Several publications revealed that the main failure mechanism of full-cells comprising a tin- or silicon-based N is the depletion of active Li caused by initial formation and continuous reformation of the SEI layer at N, due to the extreme volume changes of alloy-type N materials upon lithiation/de-lithiation.[128,134-140] This is one of the major reasons why results achieved for negative electrode materials within *Li metal cells* (here: the classical negative electrode is defined as P) cannot directly be transferred to LIB full-cells. This latter option is the most suitable choice to demonstrate practicality of negative electrode materials and will be further discussed in the next chapter, with special focus on the *three-electrode configuration.*

3.3.3 Study of "alloying"-type materials in a full-cell setup in three-electrode configuration – influence of continuous loss of active Li

Besides the implementation of a RE for *half-cell setups (three-electrode configuration)*, the RE can also serve as diagnostic tool for *full-cell setups* to display the individual electrode potentials (N and P) during charge/discharge cycling.

Several factors, which can affect individual electrode potentials within full-cells have been already discussed in previous sections. We want to focus again on the issue of electrode potential shifting related to active Li loss in this section. As described in section 3.3.1, a major failure mechanism of full-cells containing a silicon-based N, is the consumption of active Li upon cycling. **Figure 7** depicts the development of the electrode potentials of N and P upon cell voltage controlled cycling of a NCM523 || Si-Gr cell for 54 cycles, monitored *via* an external Li metal RE.[128] As result of continuous active Li consuming SEI (re-)formation at N, the end-of-charge potential of N is gradually shifted towards higher values, cf. ref.[10]. Simultaneously, under cell voltage control and keeping the cut-off upper cell voltage constant, P is forced to cycle at higher potentials resulting in higher de-lithiation degrees, which subsequently can cause P-induced capacity fading of the full-cells (*cf.* section 3.1.3). Furthermore, alloying-type N materials, like silicon, are usually mixed with carbon to achieve reasonable performance by reducing the overall volume expansion.[141] Recently, Yao *et al*. reported on the quantification of the lithiation and de-lithiation amounts of Si-graphite blends, which is of high importance as silicon and graphite cycle in different potential regions. While the lithiation begins with Si, followed by graphite at potentials below 0.2 V *vs*. Li|Li$^+$, de-lithiation starts preferentially from graphite (≈0.01-0.23 V *vs*. Li|Li$^+$), before lithium extraction from Si (≈0.23-1.00 V *vs*. Li|Li$^+$).[142] Therefore, the above-mentioned phenomenon can drive the potential of N at the end of charge to values, at which the graphite is less or even not at all involved in the lithiation process, *i.e*. >200 mV *vs*. Li|Li$^+$, hence, predominantly/only silicon is cycled thereafter. These effects demonstrate, that it is not possible to directly transfer results for negative electrode materials obtained in a *half-cell setup (three-electrode configuration),* cycled within a defined potential range, to cell voltage controlled *full-cell setups.* We want to emphasize other researches to take into account the advantages but also the issues coming along with different cell setups for the investigation of negative electrode materials and, therefore, choose the setup accordingly to the intended objective of the investigation.

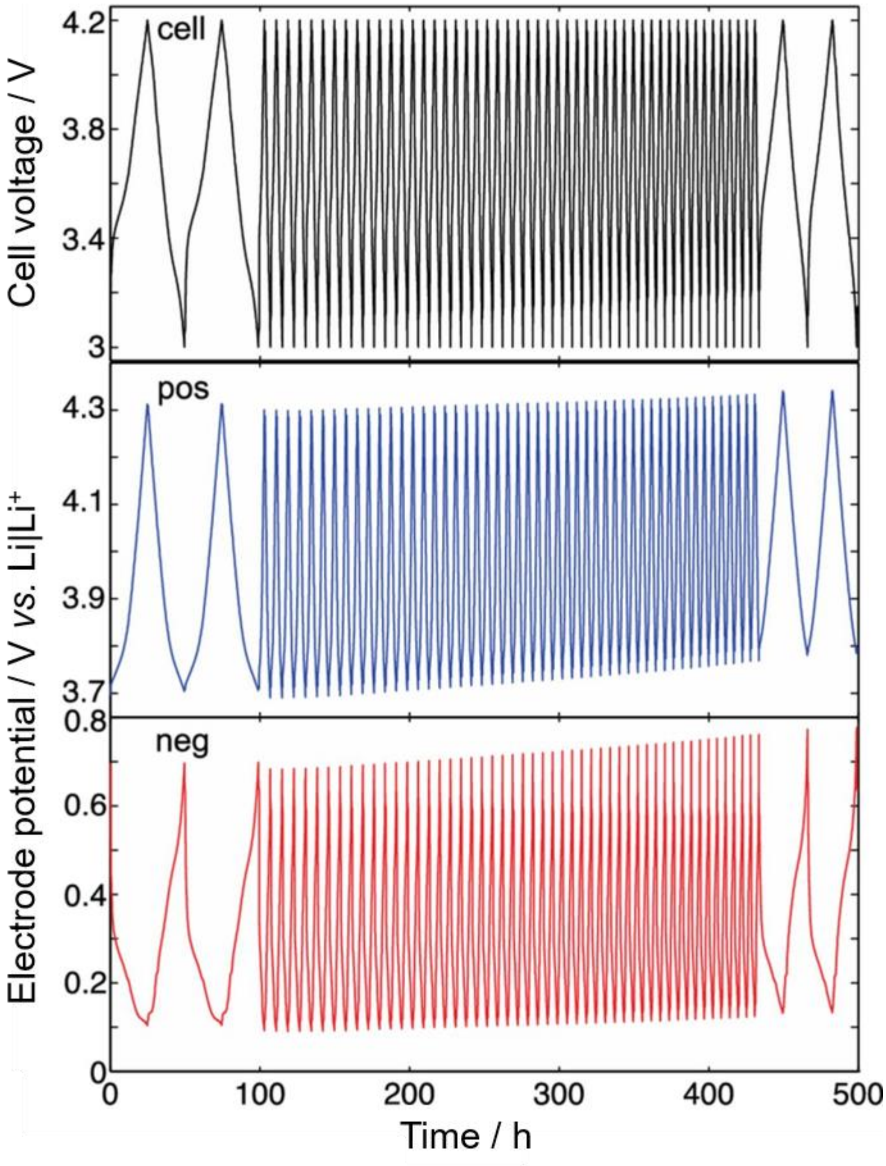

Figure 7: Development of the positive (middle) and negative electrode (bottom) potentials of a NCM523 || Si-Gr cell cycled at a fixed cell voltage (top) range of 3.0 - 4.2 V at 30 °C with a current of 0.06 mA cm^{-2} for the first and last two cycles and 0.4 mA cm^{-2} for the intermediate 50 cycles. The Si-Gr negative electrode contained 15 wt.% amorphous nano-sized silicon particles and 73 wt.% graphite, and the applied electrolyte contained 1.2 M $LiPF_6$ in EC:EMC, 3:7 w/w + 10 wt.% FEC. The individual electrode potentials were monitored *via* an external Li|Li^+ RE. Modified from ref [128].

4. Concluding remarks

Fundamental electrochemical investigations of the various LIB components, *i.e.* the negative and positive electrode materials or the electrolyte formulation, are typically performed within different cell setups (*half-cell setup*, *symmetrical-cell setup*, *full-cell setup*) in either *two-electrode* or *three-electrode configuration*. There is no clear and consequent notation of these different cell setups in the battery research community, and sometimes the terms are even incorrectly utilized, for example when the term “half-cell” is used for a Li metal-based full cell. As a result of the inconsequent usage of terms and due to the fact that often insufficient information is given about the specifically used cell setup, cell configuration and potential or cell voltage control conditions, it is not only hard to understand but also difficult to accurately compare results of different studies. Even worse, in some reports a “wrong”, *i.e.*, not suitable cell setup or configuration is chosen to address a certain scientific question, which may lead to misinterpretation of results.

In this work, we present a guide how to choose the suitable and “right” cell setup, appropriate for the intended aim of the electrochemical study. Furthermore, we encourage researchers to use the correct terms and give a clear definition about their electrochemical cell setup and configuration, which is mandatory to avoid any misinterpretations. For *half-cell setups* in *three-electrode configuration,* we recommend to use the terms working electrode (WE), counter electrode (CE) and reference electrode (RE). In such a setup, the WE potential (in V *vs*. RE) is controlled and monitored *via* a RE. In contrast, for *full-cell setups* in *two-* or *three-electrode configuration*, in which the cell voltage (in V) is controlled and monitored, we recommend to use the terms negative (N) and positive electrode (P).

A precise choice of the overall cell setup including the electrodes (either WE and CE or N and P), and a possible RE needs to be done according to the desired target of the investigation (see **Figure 8** and **Figure 9**). The selection of the opposite electrode (*e.g*. the CE in a *half-cell setup, three-electrode configuration*) plays a significant role when studying a novel material/electrode (“electrode of interest”; *e.g*. the WE) or when electrolyte/additives are investigated.

We also want to clearly point out the challenges related to the usage of a *two-electrode configuration* (*full-cell setup*) using a Li metal N for the investigation of LIB materials, *i.e.*, these considerations exclude *Li metal cells,* operated with the clear target to use Li metal negative electrodes, *e.g.* in lithium-sulfur or lithium-air cells. For the examination of a novel LIB electrode material, the exact monitoring and precise control of the electrode potential is highly important, as lithiation/de-lithiation amounts of electrode materials are electrode potential-dependent. As in a *two-electrode configuration* only the cell voltage can be controlled, overpotentials at/of Li metal, which are commonly known to evolve during dissolution/deposition of Li metal (except for a very low current density or suitable constant current-constant voltage (CCCV) cycling methods), will affect the effective potential of the electrode of interest. Additionally, in a *full-cell setup* several aspects like N/P capacity balancing inaccuracies, active Li losses or overpotentials evolving at either the N or P side can significantly affect the performance of the cell, and make it rather impossible to investigate the electrode of interest independently of the other electrode.

In the first step, *i.e.,* for the first electrochemical investigations of novel active negative and positive electrode materials , referred as "***screening***", we recommend to use a *half-cell setup* in a *three-electrode configuration* (**Figure 9 (b)**) to characterize material- and electrode-intrinsic electrochemical properties (reversible capacity, Coulombic efficiency, mechanical material/electrode stability, *etc.*, see also **Figure 8**) by excluding influences of the CE. Furthermore, an excess of active lithium is guaranteed in this initial study when Li metal is used as CE. In a second step, *i.e.*, if the investigated active material shows promising results in this *half-cell setup (three-electrode configuration),* the "***practicality***" should be evaluated with a N/P capacity balanced LIB *full-cell setup* within a *two-electrode configuration* (**Figure 9 (d)**) to demonstrate *e.g.* the long-term charge/discharge cycling performance and to evaluate the rate performance. In addition, an implementation of a RE within a *three-electrode configuration* (**Figure 9 (e)**) allows for monitoring the individual electrode potentials during cycling of the full-cell and, therefore, the observation of the origin of a possible failure "***mechanism***" (**Figure 8**). Furthermore, the electrochemical performance of the material of interest can be studied within a *symmetrical-cell setup* in *two-electrode configuration* (**Figure 9 (c)**), in which a possible cross-talk of the investigated electrode of interest and the second electrode can be excluded.

For a comprehensive investigation of novel electrolyte components and/or electrolyte additives and for demonstration of their practicality, we recommend "screening" directly in a *full-cell setup* in *two-electrode configuration* (**Figure 9 (d)**), preferably in machine-made cells to guarantee high reproducibility. This is due to the fact, that metallic Li, when used as CE or N, is highly reducing towards nearly all kinds of electrolytes/additives, making it impossible within *Li metal cells* to determine, whether the effect of the electrolyte/additive on cell performance is arising from the electrode of interest or the "auxiliary" Li metal electrode. Furthermore, to be an appropriate candidate for commercial application within LIBs, the electrolyte/additive needs to prove its beneficial effect within the *full-cell setup* with SOTA N and P materials. After a successful screening, the underlying "*mechanism", i.e.* the determination of the precise origin of the beneficial effect of the electrolyte/additive, can be investigated within a *full-cell setup* in *three-electrode configuration* (**Figure 9 (e)**) or in the *symmetrical-cell setup* (**Figure 9 (c)**).

In any case, the use of Li metal as "auxiliary" opposite electrode in all types of cell setups and cell configurations typically results in a massive excess of active Li capacity in the cell, which inevitably will alter the results compared to a practical LIB cell with capacity balanced electrodes, thus, with a capacity-limited positive electrode and a capacity-excess negative electrode.

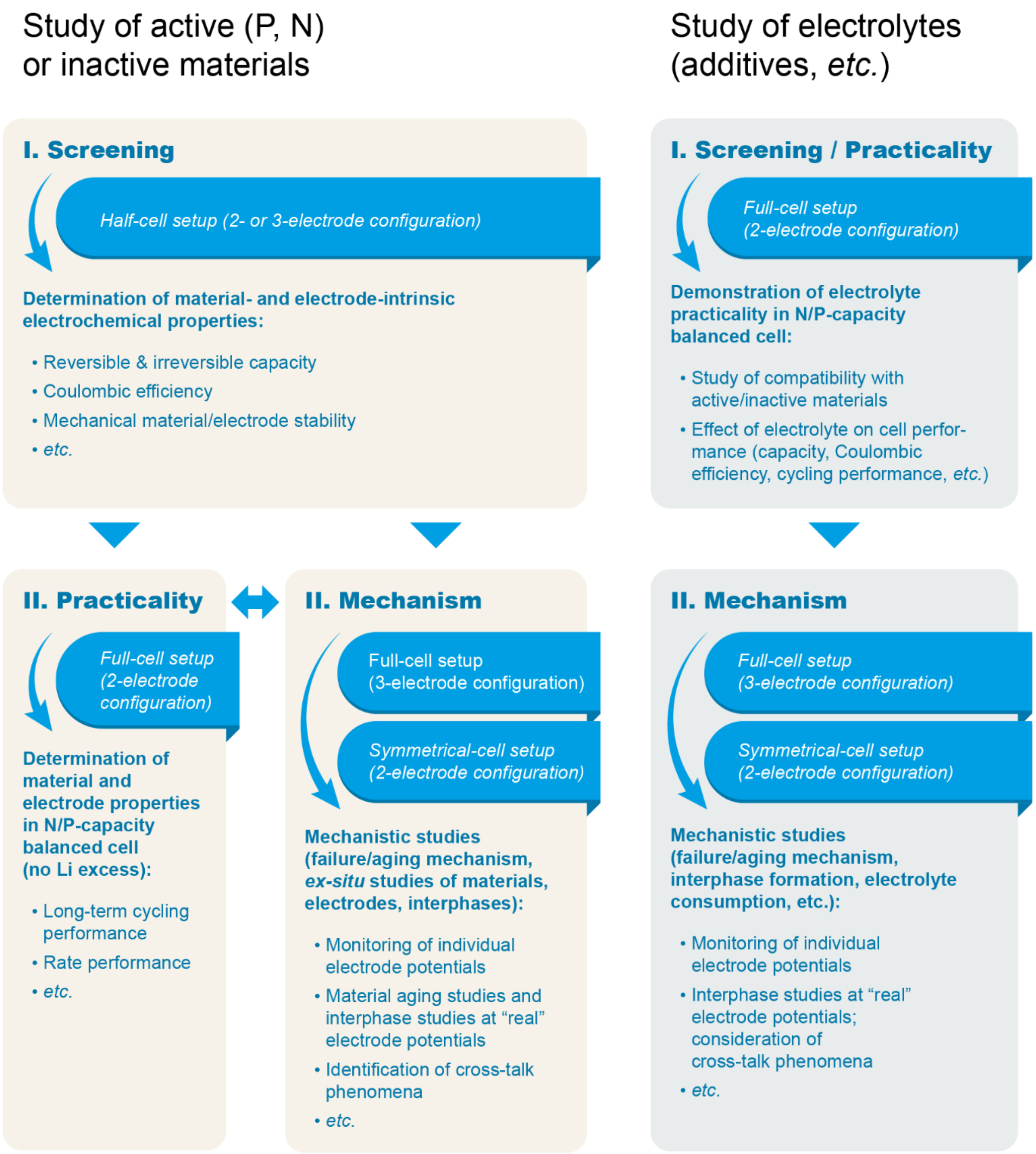

Figure 8: Proposed order for the investigation of different (electrochemical) properties of battery materials (classified within the terms "*screening*", "*practicality*" and "*mechanism*"), including the appropriate cell setup for the intended goal of investigation.

Eventually, after screening and investigation of all active and inactive components of a LIB cell in various cell setups and cell configurations, only a performance check in two-electrode LIB full cells with practical mass loading, electrolyte amounts and capacity balanced electrodes, will tell about the true impact of present and new cell chemistries. From this point of view, the considerations/conclusion in/of this review may be in most cases transferable to other battery cell chemistries.

We hope that this reality check and tutorial will help to drive the research community, especially new entrants, towards a more consistent terminology use for cell setups and measurement conditions for battery cell and battery material research. By achieving this, we anticipate to boost the battery research by directing towards more appropriate and focused electrochemical experiments, which enable better comparability between experiments of different groups and allow for more realistic conclusions and perspectives of the presented results.

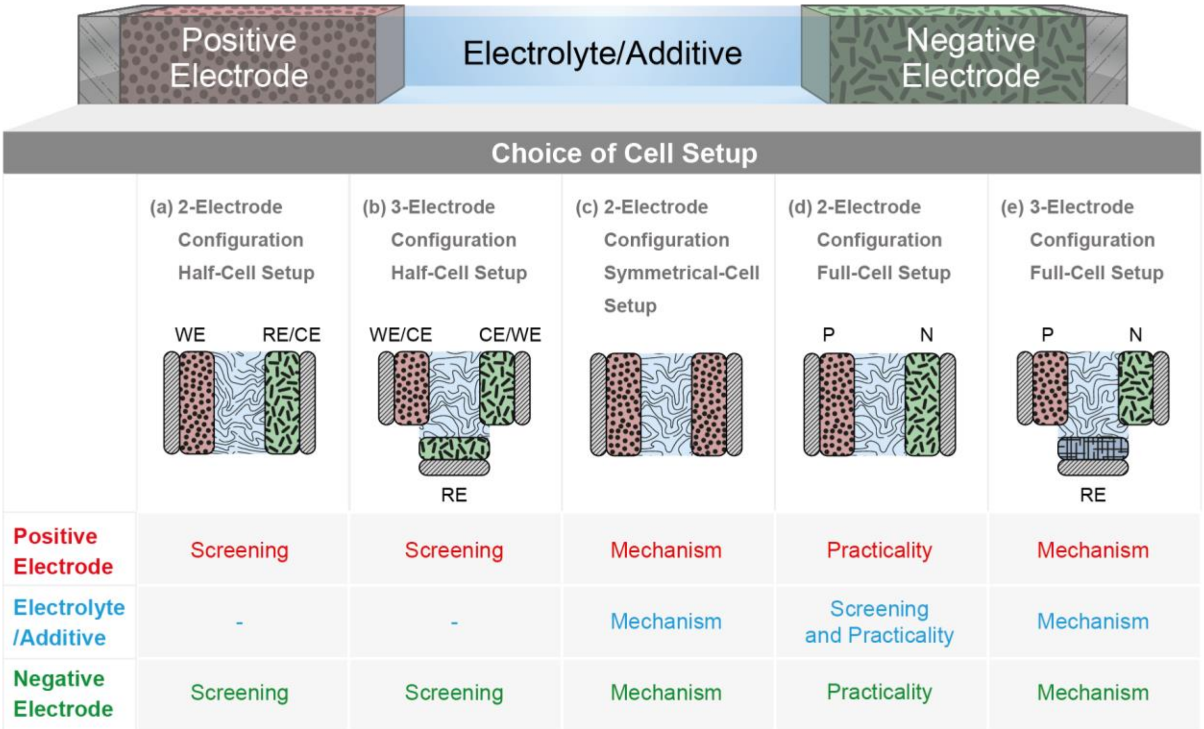

Figure 9: Proposed choice of cell setup according to the objective of the investigation of a LIB material, electrode or electrolyte formulation. For the first electrochemical investigations of new electrode materials, *i.e.*, screening, we recommend to use a *half-cell setup* in either *two-electrode configuration** (a) or *three-electrode configuration* (b). After successful screening, the practicality, *i.e.* the possible implementation within a practical LIB setup, of the new material and/or electrolyte should investigated in either a *full-cell setup* in *three-electrode configuration* (e), or in a *full-cell setup* in *two-electrode configuration* (d) or in a *symmetrical-cell setup* in *two-electrode configuration* (c). When screening novel electrolytes/additives, we suggest to utilize a *full-cell setup* in *two-electrode configuration* (d) to prove the compatibility within a practicable LIB set-up with state-of-the-art electrode materials. After selecting appropriate candidates, the working mechanism of the new electrolyte/additive

can be investigated in either a *full-cell setup* in *three-electrode configuration* (e) or in a *symmetrical-cell setup* in *two-electrode configuration* (c). *: only valid at very low current density at the CE/RE.

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Declaration of interest

None.

Data availability

The raw data required to reproduce these findings will be made available on request.

References

1. Pillot, C., The Rechargeable Battery Market and Main Trends 2017–2025, Talk and Slides at Advanced Automotive Battery Conference (AABC) Europe. Mainz(2018)
2. Schmuch, R., *et al.*, *Nature Energy* (2018) **3** (4), 267
3. Blomgren, G. E., *Journal of The Electrochemical Society* (2017) **164** (1), A5019
4. Ding, Y., *et al.*, *Electrochemical Energy Reviews* (2019)
5. Wagner, R., *et al.*, *Journal of Applied Electrochemistry* (2013) **43** (5), 481
6. Placke, T., *et al.*, *Journal of Solid State Electrochemistry* (2017) **21** (7), 1939
7. Placke, T., *et al.*, *Joule* (2018) **2** (12), 2528
8. Winter, M., *et al.*, *Chemical Reviews* (2018) **118** (23), 11433
9. Betz, J., *et al.*, *Advanced Energy Materials* (2019) **9** (6), 1803170
10. Chen, S., *et al.*, *Joule* (2018) **2** (8), 1548
11. Imholt, L., *et al.*, *ACS Macro Letters* (2018) **7** (7), 881
12. Kasnatscheew, J., *et al.*, *Topics in Current Chemistry* (2018) **376** (3), 16
13. Krueger, S., *et al.*, *Journal of the Electrochemical Society* (2013) **160** (4), A542
14. Harlow, J. E., *et al.*, *Journal of The Electrochemical Society* (2018) **165** (16), A3595
15. Winter, M., and Besenhard, J. O., *Chemie in unserer Zeit* (1999) **33** (5), 252
16. Bard, A. J., and Faulkner, L. R., *Electrochemical Methods: Fundamentals and Applications*. Wiley: 2000
17. La Mantia, F., *et al.*, *Electrochemistry Communications* (2013) **31**, 141
18. Daniel, C., and Besenhard, J. O., *Handbook of Battery Materials*. John Wiley & Sons: 2011
19. Holtstiege, F., *et al.*, *Physical Chemistry Chemical Physics* (2017) **19** (38), 25905
20. Burrows, B., and Jasinski, R., *Journal of The Electrochemical Society* (1968) **115** (4), 365
21. McTurk, E., *et al.*, *ECS Electrochemistry Letters* (2015) **4** (12), A145
22. Dolle, M., *et al.*, *Journal of the Electrochemical Society* (2001) **148** (8), A851
23. Costard, J., *et al.*, *Journal of the Electrochemical Society* (2017) **164** (2), A80

24. Tchitchekova, D., *et al.*, *Journal of The Electrochemical Society* (2017) **164** (7), A1384
25. Raccichini, R., *et al.*, *Batteries* (2019) **5** (1), 12
26. Long, B. R., *et al.*, *Journal of The Electrochemical Society* (2016) **163** (14), A2999
27. Blyr, A., *et al.*, *Journal of the Electrochemical Society* (1998) **145** (1), 194
28. Obrovac, M., and Chevrier, V., *Chemical reviews* (2014) **114** (23), 11444
29. Belt, J. R., *et al.*, *Journal of the Electrochemical Society* (2014) **161** (6), A1116
30. Nagasubramanian, G., *J Power Sources* (2000) **87** (1-2), 226
31. Uhlmann, C., *et al.*, *J Power Sources* (2015) **279**, 428
32. Klink, S., *et al.*, *Electrochemistry Communications* (2012) **22**, 120
33. Ender, M., *et al.*, *Journal of The Electrochemical Society* (2017) **164** (2), A71
34. Klink, S., *et al.*, *J Power Sources* (2013) **240**, 273
35. Hoshi, Y., *et al.*, *J Power Sources* (2015) **288**, 168
36. Raijmakers, L. H. J., *et al.*, *Electrochim Acta* (2018) **259**, 517
37. Bieker, G., *et al.*, *Physical Chemistry Chemical Physics* (2015) **17** (14), 8670
38. Becking, J., *et al.*, *Advanced Materials Interfaces* (2017) **4** (16), 1700166
39. Shen, C., *et al.*, *Journal of The Electrochemical Society* (2017) **164** (13), A3349
40. Burns, J., *et al.*, *Journal of The Electrochemical Society* (2011) **158** (12), A1417
41. Applestone, D., and Manthiram, A., *J Power Sources* (2012) **217**, 1
42. Chevrier, V. L., *et al.*, *Journal of The Electrochemical Society* (2014) **161** (5), A783
43. Kasnatscheew, J., *et al.*, *Physical chemistry chemical physics* (2016) **18** (5), 3956
44. Kasnatscheew, J., *et al.*, *Journal of The Electrochemical Society* (2017) **164** (12), A2479
45. Whittingham, M. S., *Chemical reviews* (2004) **104** (10), 4271
46. Ellis, B. L., *et al.*, *Chemistry of materials* (2010) **22** (3), 691
47. Liu, W., *et al.*, *Angewandte Chemie International Edition* (2015) **54** (15), 4440
48. Goodenough, J. B., and Kim, Y., *J Power Sources* (2011) **196** (16), 6688
49. Kasnatscheew, J., *et al.*, *Energy Technology* (2017) **5** (9), 1670
50. Kasnatscheew, J., *et al.*, *Journal of The Electrochemical Society* (2016) **163** (14), A2943
51. Manthiram, A., *et al.*, *Solid State Ionics* (2006) **177** (26-32), 2629
52. He, P., *et al.*, *Journal of Materials Chemistry* (2012) **22** (9), 3680
53. Kasnatscheew, J., *et al.*, *The Journal of Physical Chemistry C* (2017) **121** (3), 1521
54. Kasnatscheew, J., *et al.*, *J Power Sources* (2017) **359**, 458
55. Winter, M., *Zeitschrift für physikalische Chemie* (2009) **223** (10-11), 1395
56. Peled, E., and Menkin, S., *Journal of The Electrochemical Society* (2017) **164** (7), A1703
57. Buqa, H., *et al.*, *Ionics* (2000) **6** (3-4), 172
58. Kasnatscheew, J., *et al.*, *J Power Sources* (2017) **362**, 278
59. Hilbig, P., *et al.*, *Current Topics In Electrochemistry* (2018) **20**, 1
60. Kasnatscheew, J., *et al.*, *Physical Chemistry Chemical Physics* (2017) **19** (24), 16078
61. Betz, J., *et al.*, *Advanced Energy Materials* (2019) **9** (21), 1900574
62. Xu, K., *Chemical reviews* (2004) **104** (10), 4303
63. Schmitz, R. W., *et al.*, *Progress in Solid State Chemistry* (2014) **42** (4), 65
64. Zhang, S. S., *J Power Sources* (2006) **162** (2), 1379
65. Xu, K., *Chemical reviews* (2014) **114** (23), 11503
66. Haregewoin, A. M., *et al.*, *Energy & Environmental Science* (2016) **9** (6), 1955
67. Flamme, B., *et al.*, *Green Chemistry* (2017) **19** (8), 1828
68. Gallus, D. R., *et al.*, *Electrochim Acta* (2015) **184**, 410
69. Qian, Y., *et al.*, *J Power Sources* (2016) **329**, 31
70. Xu, M., *et al.*, *Electrochemistry communications* (2012) **18**, 123
71. Mai, S., *et al.*, *J Power Sources* (2015) **273**, 816
72. Barghamadi, M., *et al.*, *J Power Sources* (2015) **295**, 212
73. Heine, J., *et al.*, *Journal of The Electrochemical Society* (2015) **162** (6), A1094

74. Wu, F., *et al.*, *Advanced Materials* (2015) **27** (1), 101
75. Zheng, J., *et al.*, *Nature Energy* (2017) **2**, 17012
76. Winter, M., *et al.*, *Monatshefte für Chemie / Chemical Monthly* (2001) **132** (4), 473
77. Vogl, U. S., *et al.*, *Journal of The Electrochemical Society* (2015) **162** (12), A2281
78. Nie, M., *et al.*, *The Journal of Physical Chemistry C* (2013) **117** (3), 1257
79. Qian, Y., *et al.*, *J Power Sources* (2016) **332**, 60
80. Rodrigues, M.-T. F., *et al.*, *Journal of The Electrochemical Society* (2018) **165** (9), A1697
81. Smith, A., *et al.*, *Journal of The Electrochemical Society* (2011) **158** (10), A1136
82. Björklund, E., *et al.*, *Journal of The Electrochemical Society* (2017) **164** (13), A3054
83. Xiong, D., *et al.*, *Journal of The Electrochemical Society* (2016) **163** (3), A546
84. Michalak, B., *et al.*, *The Journal of Physical Chemistry C* (2016) **121** (1), 211
85. Kleiner, K., *et al.*, *J Power Sources* (2016) **317**, 25
86. Xiong, D., *et al.*, *Journal of The Electrochemical Society* (2017) **164** (2), A340
87. Krause, L., *et al.*, *Journal of The Electrochemical Society* (2017) **164** (12), A2527
88. Gyenes, B., *et al.*, *Journal of The Electrochemical Society* (2015) **162** (3), A278
89. Petibon, R., *et al.*, *Journal of The Electrochemical Society* (2016) **163** (13), A2571
90. Hall, D. S., *et al.*, *Journal of The Electrochemical Society* (2019) **166** (4), A793
91. Hall, D. S., *et al.*, *Journal of The Electrochemical Society* (2018) **165** (13), A2961
92. Hall, D. S., *et al.*, *Journal of The Electrochemical Society* (2018) **165** (10), A2365
93. Ellis, L., *et al.*, *Journal of The Electrochemical Society* (2017) **164** (14), A3518
94. Murray, V., *et al.*, *Journal of The Electrochemical Society* (2019) **166** (2), A329
95. Dagger, T., *et al.*, *J Power Sources* (2018) **396**, 519
96. Long, B. R., *et al.*, *Journal of The Electrochemical Society* (2016) **163** (14), A2999
97. Marks, T., *et al.*, *Journal of The Electrochemical Society* (2011) **158** (1), A51
98. Beltrop, K., *et al.*, *Chemistry of Materials* (2018) **30** (8), 2726
99. Tornheim, A., *et al.*, *Journal of The Electrochemical Society* (2017) **164** (1), A6366
100. Abraham, D., *et al.*, *Electrochim Acta* (2005) **51** (3), 502
101. Ohzuku, T., *et al.*, *Journal of the Electrochemical Society* (1995) **142** (5), 1431
102. Petibon, R., *et al.*, *J Power Sources* (2014) **251**, 187
103. Petibon, R., *et al.*, *Journal of The Electrochemical Society* (2014) **161** (1), A66
104. Petibon, R., *et al.*, *Journal of the Electrochemical Society* (2013) **160** (1), A117
105. Chen, C., *et al.*, *J Power Sources* (2001) **96** (2), 321
106. Plashnitsa, L. S., *et al.*, *Electrochim Acta* (2011) **56** (3), 1344
107. Nowak, S., and Winter, M., *Journal of The Electrochemical Society* (2015) **162** (14), A2500
108. Evertz, M., *et al.*, *J Power Sources* (2016) **329**, 364
109. Gallus, D. R., *et al.*, *Electrochim Acta* (2014) **134**, 393
110. Komaba, S., *et al.*, *Electrochim Acta* (2002) **47** (8), 1229
111. Zhan, C., *et al.*, *Nature communications* (2013) **4**, 2437
112. Zhan, C., *et al.*, *Advanced Materials Interfaces* (2016) **3** (11), 1500856
113. Banerjee, A., *et al.*, *Journal of The Electrochemical Society* (2017) **164** (1), A6315
114. Banerjee, A., *et al.*, *Journal of the American Chemical Society* (2017) **139** (5), 1738
115. Jung, R., *et al.*, *The journal of physical chemistry letters* (2017) **8** (19), 4820
116. Gilbert, J. A., *et al.*, *Journal of The Electrochemical Society* (2017) **164** (2), A389
117. Meister, P., *et al.*, *Chemistry of Materials* (2016) **28** (20), 7203
118. Jia, H., *et al.*, *2016* (2016) **63** (3), 14
119. Bresser, D., *et al.*, *Advanced Energy Materials* (2013) **3** (4), 513
120. Jia, H., *et al.*, *ACS applied materials & interfaces* (2015) **7** (3), 1508
121. Li, X., *et al.*, *Nature communications* (2014) **5**, 4105
122. Wu, H., *et al.*, *Nano letters* (2012) **12** (2), 904

123. Ge, M., *et al.*, *Nano letters* (2012) **12** (5), 2318
124. Chae, S., *et al.*, *Joule* (2017) **1** (1), 47
125. Heine, J., *et al.*, *Advanced Energy Materials* (2014) **4** (5), 1300815
126. Cohen, Y. S., *et al.*, *The Journal of Physical Chemistry B* (2000) **104** (51), 12282
127. Brissot, C., *et al.*, *J Power Sources* (1999) **81**, 925
128. Klett, M., *et al.*, *Journal of The Electrochemical Society* (2016) **163** (6), A875
129. Wetjen, M., *et al.*, *Journal of The Electrochemical Society* (2017) **164** (12), A2840
130. Dose, W. M., *et al.*, *Journal of The Electrochemical Society* (2018) **165** (10), A2389
131. Dose, W., *et al.*, *Chemical Communications* (2018) **54** (29), 3586
132. Wetjen, M., *et al.*, *Journal of The Electrochemical Society* (2018) **165** (10), A2340
133. Wetjen, M., *et al.*, *Journal of The Electrochemical Society* (2018) **165** (7), A1503
134. Bareño, J., *et al.*, *The Journal of Physical Chemistry C* (2017) **121** (38), 20640
135. Delpuech, N., *et al.*, *ChemSusChem* (2016) **9** (8), 841
136. Dupré, N., *et al.*, *Chemistry of Materials* (2016) **28** (8), 2557
137. Trask, S. E., *et al.*, *Journal of The Electrochemical Society* (2016) **163** (3), A345
138. Nölle, R., *et al.*, *ACS applied materials & interfaces* (2018) **10** (33), 28187
139. Wachtler, M., *et al.*, *J Power Sources* (2001) **94** (2), 189
140. Winter, M., *et al.*, Studies on the Anode/Electrolyte Interface in Lithium Ion Batteries. In *Electroactive Materials*, Besenhard, J. O., *et al.*, (eds.) Springer Vienna, Vienna, (2001), pp 53
141. Hochgatterer, N. S., *et al.*, *Electrochemical and Solid-State Letters* (2008) **11** (5), A76
142. Yao, K. P. C., *et al.*, *Advanced Energy Materials* (2019) **9** (8), 1803380