

Self-discharge of Batteries: Causes, Mechanisms and Remedies

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Abstract: Self-discharge¹ of batteries is a natural, but nevertheless quite unwelcome phenomenon. Because it is driven in its various forms by the same thermodynamic forces as the discharge during intended operation of the device it can only be slowed down by impeding the reaction kinetics of its various steps, i.e. their respective rates of reaction. This approach should be based on a deeper understanding of the various modes and mechanisms of self-discharge, which in turn depends on the battery chemistry, its mode of operation and environmental conditions. Typical examples from representative battery chemistries are presented and observed effects are reviewed. Similarities between battery chemistries and causes of self-discharge are identified; concepts and ideas obtained this way are outlined. As an outcome of a better understanding of both common and system-independent causes and mechanisms of self-discharge as well as chemistry-specific processes approaches to reduce self-discharge are presented. Achieved progress is highlighted.

Keywords: Energy storage; Electrochemical energy conversion; Batteries; Accumulators; Flow batteries

1. Introduction

A secondary battery fully charged up to its rated capacity would ideally keep the energy stored in chemical compounds for infinite periods of time (i.e. infinite charge retention time); a primary

battery would keep the electric energy stored during its production in the form of chemical compounds also without any loss indefinitely. Unfortunately reality looks different, but because a secondary battery can be recharged (trickle charge, provided a source of electric

¹During the literature review the somewhat unusual spelling self discharge was encountered infrequently.



energy is available), whereas a primary battery cannot be recharged, the problem of self-discharge appears to be more urgent with the latter.

A fresh primary battery and a charged secondary battery are in thermodynamic terms in an energetically higher state, i.e. the corresponding absolute value of free enthalpy (Gibbs energy) is larger. Because discharge is a spontaneous process the values carry a negative sign, accordingly describing statements must take this into account. This charged state is far away from thermodynamic equilibrium. The device strives to attain an equilibrium state where the free enthalpy is equal to zero in the discharged state, wherein the driving force for discharge and release of electric energy is exhausted. In addition to the intended way to move into this state by controlled discharge further ways are conceivable and unfortunately operative in most cases, they are summarized as self-discharge. The latter is highly unwelcome, but given the thermodynamic facts self-discharge it can only be slowed down as good as possible, i.e. kinetics of processes causing self-discharge should be slowed down as good as possible. This applies primarily to chemical reactions contributing to self-discharge; in addition parasitic currents with non-thermodynamic causes can contribute to self-discharge.

Because self-discharge can be described from an electrical engineering point of view as the flow of an unwanted current the operating chemical and electrical effects and descriptions can be summarized into the wish to minimize this unwanted current(s). In an equivalent circuit representation of a cell this current can be represented as a shunt resistor, the current is sometimes called leak current. This has been extensively applied in modeling of self-discharge of supercapacitors^[1]. This general concept does not apply to all forms of self-discharge. Unwanted processes like destruction and reformation of layers on the electrode having the same effect as common self-discharge processes are included here although they are essentially different.

Parasitic electric currents not related to chemical processes hardly depend on type of battery (primary or secondary) and battery chemistry (aqueous or non-aqueous electrolyte solution); they will be discussed jointly in a section below. Chemical processes causing self-discharge strongly depend on battery chemistry, beyond the type of electrolyte solution also very much on electrode materials. In following two sections

examples will be discussed assigned to the two types of electrolyte solutions (frequently the term electrolyte is used in a way which appears to include the term electrolyte solution; this saves a word but possibly causes confusion. In addition it oversimplifies the meaning of electrolyte^[2,3]). Redox flow batteries based on a very different mode of operation^[2,4] are treated in a separate section. Options to remedy self-discharge or to keep it as low as possible are similar for both aqueous and non-aqueous electrolyte solutions, they are treated jointly in a final section. In the preceding sections only very specific options to reduce self-discharge are discussed. First a general overview will be provided.

The particular importance of self-discharge in setups for energy harvesting with supercapacitors and lithium-ion batteries as storage devices has been examined elsewhere^[5].

2. A General Overview

The energy that can be retrieved from a cell - even when carefully taking into account limited efficiencies caused by overpotentials and other, in part kinetic, effects - will decrease as a function of the duration of storage (shelf time). For some systems this loss will be hardly noticeable (shelf times of ten and more years are claimed for some systems with losses in the range of a few percents per year only^[2,6]) or will be almost complete already after a few months or even less. These losses tend to be more pronounced at elevated temperatures. Because of the mostly complicated and sometimes only partially known reactions predictions of temperature dependency of self-discharge are difficult. Instead empirical data yielding **Figure 1** have been collected.

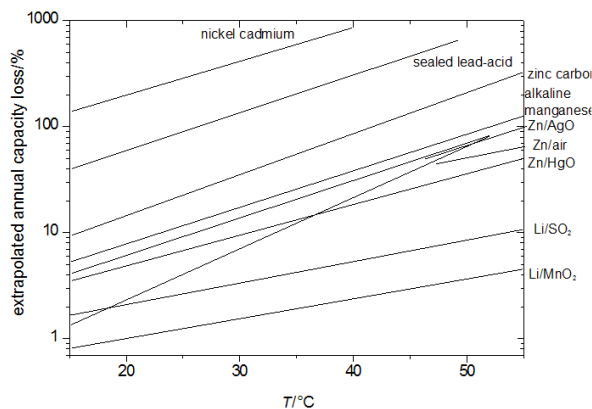


Figure 1. Extrapolated annual capacity losses of selected primary and secondary systems (Based on data in ref. [2])

The sometimes very significant temperature effects, i.e. accelerating self-discharge with increasing temperature, make it e.g. impossible to fully charge a nickel-cadmium battery at temperatures $T > 60$ °C because self-discharge becomes faster than the desired charging reactions.

Because these disappointing results are similar to the results of intended and proper use (i.e. discharge), this phenomenon is called self-discharge. Strictly speaking the term applies only to complete (sometimes misleadingly called full) cells; to self-discharge a single electrode does not make sense. Because many studies of self-discharge focus on processes just at one electrode sometimes the term is applied in an expanded meaning, below such studies are included. Self-discharge's many causes differ fundamentally. Parasitic electric currents along electronically conducting electric pathways between the battery poles inside or outside of the cell may cause self-discharge (see section 3). Currents due to stand-by functions of the device energized by the battery also drain a current from the cell, but they are commonly not discussed in the present context. But more frequent reasons of self-discharge are chemical reactions between active masses and constituents of the electrolyte solution. In case of a primary lithium battery (lithium metal battery LMB) the negative electrode (anode) is stable only because it coats itself with a protective layer of electronically insulating material (solid electrolyte interphase SEI, see below in section 5) suppressing or at least slowing down further chemical reactions between the lithium metal (which is thermodynamically unstable versus basically every electrolyte solution) and its nonmetallic environment. Formation of this SEI consumes some lithium - and the result is a loss of stored energy: self-discharge. During operation the SEI may be partially removed and lost, it must be restored when the load is disconnected and flow of current stops. Again a loss of lithium happens; correspondingly some energy has become unavailable. The same applies to the negative graphite acting as a host for lithium in lithium-ion batteries. The reactions may also simply be called corrosion, but this term would look somewhat out-of-place here. In case of the lead-acid battery it may look more appropriate. Lead being less noble than hydrogen reacts slowly with the battery acid releasing tiny amounts of hydrogen and lead ions. Again stored energy is lost. During charging the dissolved lead ions may be redeposited, but the released hydrogen cannot

be recovered easily (see section 4 for options to mitigate or circumvent this problem). A similar problem is encountered with the nickel electrode. NiOOH can react with water (of the alkaline electrolyte solution) yielding oxygen and causing lost stored energy.

All reactions associated with self-discharge are chemical or electrochemical reactions. Accordingly rate laws of chemical reaction kinetics apply - and this includes in particular the effect of temperature as already illustrated in **Figure 1**.

Because most electrochemical storage and conversion systems are thermodynamically inherently unstable or contain compounds therein which are unstable with respect to others, self-discharge is an inherent feature of them, it can only be suppressed as good as possible. Proper cell design and careful selection of materials with well defined properties and composition have helped frequently to reduce self-discharge. Self-discharge of secondary cells tends to be faster with older cells and after extensive cycling. This can at least in part be due to the formation of electrode reaction products acting as catalysts for unwanted reactions causing self-discharge or degradation of added inhibitors (as present e.g. in the electrolyte solution of alkaline batteries). High-power cells show generally higher self-discharge than high-energy cells (provided a given cell chemistry is available in both forms as reported for lithium-SOCl₂-cells); the former cells show higher self-discharge because they contain electrodes with higher surface area and thus more locations for heterogeneous self-discharge processes.

Typical self-discharge data are collected in **Table 1**.

Table 1. Typical self-discharge rates at room temperature
(Data from ref. [2])

Class	System	Self-discharge
Primary	Alkali-Manganese cell	0.5% per month
	Leclanché cell	0.5% per month
	Lithium	0.5% per month
	Lithium/iodine	< 10% per decade
	Lithium-ion	4% per month
Secondary	NiMH	25% per month
	LSD-NiMH	4% per month
	NiCd	20% per month
	RAM	0.5% per month
For comparison: supercapacitor	EDLC	1.8% per day

LSD: low self-discharge; RAM: rechargeable alkali-manganese; EDLC: electrochemical double layer capacitor

Only when the reactive compounds are separated completely no self-discharge will be possible, this can be achieved with reserve batteries or e.g. by draining the electrolyte solutions from a redox flow battery^[2].

Given the omnipresence of self-discharge with devices for electrochemical energy storage it surprises slightly that review reports, in particular current ones, on this topic are impossible to find. Certainly the term shows up frequently in abstracts and research reports on such devices. In most cases low self-discharge is claimed for a given device or even a material (although the term seems to be hardly applicable in the latter case). But frequently neither the exact way this claim was verified nor the reason for this improvement are provided. In textbooks self-discharge is addressed^[2], but even in major monographs it is mentioned only briefly^[7-11] in mostly descriptive ways without too much attention to details in particular of mechanisms and ways of slowing it down. Major reference works provide at least some access to further reading^[6,12,13], collections of research reports and reviews again provide some hints^[14,15]. Self-discharge of supercapacitors has been extensively reviewed elsewhere^[1], because of the apparent merger of secondary batteries and supercapacitors at all levels from the mode of operation and the used materials up to device types^[16,17] some overlaps with the present report are likely.

Self-discharge can also be classified into reversible and irreversible one^[14]. In the former case lost energy is restored during a subsequent recharging of the battery, this applies to self-discharge by parasitic currents or some cases of chemical self-discharge reactions. The second, less clearly defined class contains processes wherein material is either irreversibly lost or damaged (e.g. lithium lost in formation of SEI). This classification is not used here.

3. Self-discharge by Parasitic Currents

A simple cause of this form of self-discharge may be the flow of an electric current even when the device operated with the battery is switched off due to leakage by e.g. electronically slightly conducting traces of dirt on the battery surface or the battery holder or inside the battery as schematically depicted in **Figure 2**.

This flow of current may also proceed inside the cell because of incompletely insulating separators

or parasitic electric contacts between active masses (**Figure 2**). Because the current “leaks” between the electrodes via unintended Ohmic conduction pathways (thus its name leakage current) it can be represented as an external shunt resistor in parallel to the cell, this helps in modeling. Obviously these types of self-discharge can be suppressed by careful design and operation of the cell and its environment. A standby function may also draw a small current without explicit knowledge of the user; this may be considered in a broader sense also as self-discharge but is obviously beyond the scope of this review.

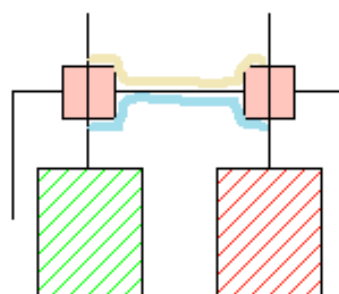
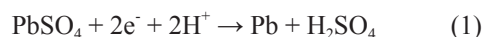


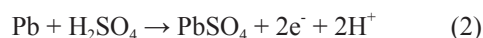
Figure 2. Parasitic currents between battery poles by conducting coatings inside and outside a cell

4. Self-discharge in Aqueous Batteries

In a secondary battery energy is stored by using electric energy to drive a chemical transformation, the obtained materials are “richer in energy” (the absolute value of the Gibbs energy or free reaction enthalpy is larger) than the starting materials in the discharged device. As an example, the charging reaction at the negative electrode of a lead-acid battery shall be considered:



Upon discharge the process is reversed:



As an alternative the following reaction is conceivable:

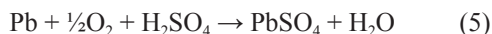


The reaction at the positive electrode can be:



Although lead is less noble than hydrogen reaction (3) is slow because lead is a poor electrocatalyst for hydrogen evolution, a similar argument applies to the positive electrode (reaction (4)), which thermodynamically is also not stable versus the electrolyte solution^[18]. Dioxygen present in the electrolyte solution of open cells can react

at the negative electrode according to



In chemical terms this can be called corrosion, in a battery this is a loss of energy and only welcome as a measure limiting hydrogen evolution during overcharge in valve-regulated lead-acid batteries (VRLA). Otherwise it is self-discharge. The rates of the mentioned reactions depend on temperature and acid concentration; with higher temperature and acid concentration the rates increase. The rate also depends on the state-of-charge (SoC). A fully charged VRLA cell may self-discharge from 100% to 90% SoC within one to two weeks, whereas at this temperature self-discharge from 20% to 10% may last ten or more weeks^[6]. Self-discharge is lower in sealed cells with a small amount of phosphoric acid added into the sulfuric acid electrolyte solution (the cells are of the “starved type”, there is no free solution)^[19]. The slower self-discharge is attributed to the presence of phosphoric acid, the expander in the negative electrode does not affect self-discharge, the antimony-free grids show corrosion, i.e. self-discharge, only at cell voltages > 2 V.

Electrochemically active impurities in the electrodes and/or the electrolyte solution like $\text{Fe}^{2+}/\text{Fe}^{3+}$ -ions may establish a redox shuttle mechanism as depicted in **Figure 3**.

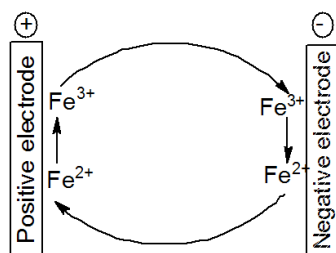
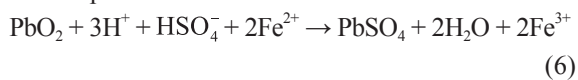


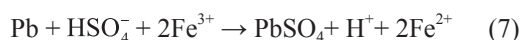
Figure 3. Scheme of an iron ion redox shuttle mechanism

The following reactions result in self-discharge:

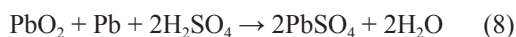
At the positive electrode:



and at the negative electrode:



yielding the cell reaction:



The cell reaction is the already stated process during regular discharge. Both parasitic electrode reactions

proceed as long as the respective electrode potentials enable them. The impurity ions themselves are not consumed; the undesired process may go on. Once discharge goes on the electrode potentials move closer to each other, consequently the electrode potential may not be favorable that much for the parasitic reactions anymore. Additives to electrodes and/or electrolyte solutions (like the expanders in lead-acid batteries) may decompose during operation leaving products which either act as catalysts for reactions like hydrogen evolution contributing to self-discharge or may establish shuttle mechanisms as depicted in **Figure 3**. Antimony alloyed into the grid for the positive electrode in a lead-acid battery may corrode and get into the battery electrolyte solution being finally deposited onto the negative electrode. There it catalyses hydrogen evolution thus decreasing charging efficiency and increasing self-discharge. Instead of antimony calcium has been suggested resulting in lower gas evolution and self-discharge^[6,11], but this substitution comes with new problems because of the now lost other beneficial effects of alloyed antimony^[6].

The state of charge and consequently self-discharge of a nickel oxide can be monitored with electrochemical impedance measurements^[20]. Exposure to hydrogen results in faster self-discharge. NiOOH used as the positive electrode in several aqueous secondary batteries is a good mixed-ion conductor readily establishing equilibrium with its aqueous environment^[7]. The reaction with water results in incorporation of hydrogen into the electrode and oxygen evolution:



The electrode potential decreases, self-discharge occurs.

The highly oxidizing capabilities of positive electrode materials like PbO_2 or nickel oxide may result in chemical oxidation of cell components like the separator yielding decomposition products and loss of energy (self-discharge). Separators made of polyamide (Nylon[®]) may also be decomposed by oxygen and hydrogen in the cell^[6]. Use of other more stable polymers, e.g. a composite of polypropylene and polyethylene with some surface treatment, help in reducing self-discharge^[6].

Lower self-discharge of NiMH-batteries has been observed with cobalt-free negative electrode materials replacing the conventional AB5-type alloys^[21]. Such alloys containing vanadium may support self-discharge

because of the solubility of vanadium enabling establishment of a redox shuttle process and associated self-discharge^[6], further details of reduced self-discharge have been reviewed^[6].

The iron electrode suggested for various secondary cells (e.g. the Fe-Ni-cell) shows significant corrosion resulting in self-discharge of the assembled cell because of its electrode potential lower than that of the hydrogen electrode^[22]. In addition to fast self-discharge, Coulombic efficiency during charging is low because of the competing hydrogen evolution^[23-26]. Because of the basically attractive features of the iron electrode attempts to mitigate self-discharge have been reported.

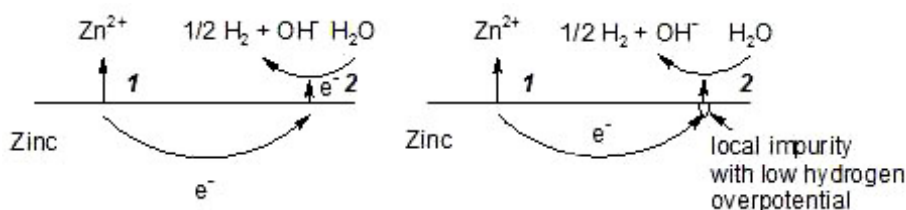


Figure 4. (a): Scheme of reactions during corrosion, i.e. self-discharge, of a zinc electrode in an aqueous electrolyte solution, with possibilities to limit it; (b): Effects of localized impurities on corrosion and self-discharge; 1: Slowing down zinc oxidation (the anodic partial reaction) and dissolution; 2: Slowing down hydrogen evolution (the cathodic partial reaction)

In primary cells this has been a major challenge with all types of zinc battery chemistries as discussed above. Some positive electrode materials like HgO used earlier in primary batteries show some solubility in the alkaline electrolyte solution resulting in deposition of mercury at the negative electrode and associated self-discharge by corresponding oxidation of metallic zinc^[28]. This deposit subsequently slows down hydrogen evolution (**Figure 4a option 2**, for obvious reasons this process is sometimes called gassing) and thus self-discharge by zinc corrosion as an initially unexpected beneficial effect. Until the ban of the use of mercury in batteries this was a common additive, now this is history. Use of high-purity zinc electrode material enabling much lower corrosion (and thus self-discharge) has been one remedy^[6,29]. Alloying with bismuth, indium, lead, or calcium has been considered as a further option^[6,29], hydrogen overpotential is increased with some alloying elements like lead (**Figure 4b option 2**). A third possibility is the addition of corrosion inhibitors (e.g. organic compounds like polyethylene glycol) to the electrolyte solution^[29-31]. These compounds may influence both options 1 and 2 (**Figure 4b**), but in

Addition of FeS and PbS has resulted in increased storage capacity and inhibition of self-discharge, 1 wt% of PbS was most effective^[27]. Formation of metal sulfites which in turn inhibit hydrogen formation and the presence of lead were identified as the causes.

Zinc employed as a negative electrode in several primary batteries with aqueous electrolyte solutions shows corrosion caused by its electrode potential negative to that of the hydrogen electrode^[22]. This basically causes hydrogen evolution, i.e. self-discharge.

Figure 4a shows schematically the various options for slowing down corrosion, i.e. self-discharge.

most cases hydrogen evolution is slowed down. Higher purity of zinc has some other advantage: It diminishes the formation of “local elements” (short-circuit cells, **Figure 4b**) of foreign metal particles embedded in zinc. Hydrogen evolution might proceed at the foreign metal with a lower hydrogen overpotential, zinc dissolution happens at the zinc surface.

A secondary zinc-air battery with a negative solid zinc electrode faces the same common problems encountered with this metal in aqueous electrolyte solutions in primary batteries. In a zinc-air cell remedies suitable for this type of cell are required. Coating the negative zinc electrode with polyaniline for use in a cell with a gelled aqueous KOH-electrolyte solution has been examined successfully^[32]. Prevention of the direct contact between the zinc electrode and the aqueous electrolyte solution afforded by the layer of PANI has been identified as major task of this coating^[33]. A quaternary ammonium functionalized polyvinyl alcohol membrane as almost neutral electrolyte was employed in a solid state zinc-air battery with much reduced self-discharge^[34]. Dendritic deposition of zinc causes several detrimental effects^[35]. Dendrites may in the extreme case penetrate the separator,

contact the positive electrode and cause a short-circuit. Less dramatic is the associated increase of surface area by this shape change with enhanced self-discharge.

A further application option for the zinc electrode has been described in a self-stratified battery with a negative zinc electrode at the bottom, an aqueous electrolyte solution on top and an organic electrolyte solution with an organic redox system insoluble in the aqueous solution and a porous carbon electrode as current collector. For improved electrode kinetics and thus higher current capability the carbon electrode is rotating^[36]. Low self-discharge is attributed to elimination of any redox shuttle due to immiscibility of the two electrolyte solutions and vastly different solubility's of the redox components in them. The cell concept goes back to the crowfoot cell popular in the 19th century with American and British telegraph companies.

The use of aluminium as a basically attractive negative electrode material with aqueous electrolyte solutions has been hampered by its instability in such solutions given by its negative electrode potential driving hydrogen evolution by corrosion. Additives to electrolyte solutions, alloying with several further elements^[6,37] with their mode of operation being the same as discussed above for the zinc electrode and replacement of the aqueous solution have been suggested.

Modeling of self-discharge has been applied to a nickel-hydrogen cell for a better understanding of ongoing processes and for prediction of cell behavior^[38]. A set of equations describing in particular the electrode reactions based on either electrode and cell parameters or assumptions of some system property values was employed. Satisfactory prediction of actual cell behavior could be obtained identifying hydrogen oxidation at the nickel electrode and oxygen evolution at this electrode as relevant processes with the first process dominating the rapid self-discharge of nickel-hydrogen cells.

5. Self-discharge in Non-aqueous Batteries

When the reduction potential of the negative electrode material and/or the oxidation potential of the positive electrode material (the respective terms anode and cathode may work in case of a primary battery, they become confusing when inspecting a secondary

battery and should thus be avoided as suggest by Huggins years ago^[7,8]) are outside the window of electrochemical stability of the electrolyte or the electrolyte solution (for a critical examination of this concept see^[39]) decomposition either of the solvent and/or the electrolyte (salt) may proceed at the positive and/or negative electrode. The effect will be self-discharge. In a few cases materials can be used with aqueous electrolyte solutions nevertheless provided the respective reactions are very slow (see above, lead acid battery negative electrode, zinc battery negative electrode).

In most cases this solution, which is actually not a solution but just tinkering, is not applicable. Primary and secondary batteries with alkali metal negative electrodes, which can decompose the electrolyte (solution) reductively, are the most popular examples. Various metal oxides are the popular corresponding example at the positive electrode, on their surface layers are formed this time by oxidation processes. Nonaqueous electrolyte solutions employing suitable organic or inorganic solvents, ionic liquids, gelled electrolyte or solid electrolytes are the frequently applied option avoiding problems associated with aqueous electrolyte solutions. Even many of these non-aqueous ionically conducting systems are thermodynamically not stable with respect to the negative electrode as well as to many highly oxidizing positive electrode materials. Because of the high reactivity of these electrode materials and the correspondingly large driving forces of both the wanted discharge reactions as well as the unwelcome self-discharge reactions slow kinetics are no solution because such slow-down would affect both self-discharge (desired) and discharge reaction (undesired). Instead protective layers are formed which separate the active material from the electrolyte (solution). The solid electrolyte interphase layer (SEI) formed on the surface of a lithium electrode is a classical example. It is the result of reductive decomposition of various components of the electrolyte solution, the actual composition and its properties have been the subject of intense research as reviewed elsewhere^[40-42], for some typical insights see^[43]. Some positive electrode materials are also capable of decomposing electrolyte solution constituents resulting in the formation of a layer (CEI, cathode electrolyte interphase), this

phenomenon has been studied less frequently, reviews are available^[44,45]. In a typical study of a CEI on copper nitroprusside $\text{Cu}[\text{Fe}(\text{CN})_5\text{NO}]$ several electrolyte solution decomposition products were identified^[46]. CEI's will have growing importance with high-voltage cells using positive electrode materials with ever higher oxidation capability.

Formation of these layers, which may also form with other ionically conducting phases between the electrodes as mentioned above consumes active material, it is thus self-discharge. Fortunately it will happen only once when the active masses are brought into contact with the electrolyte solution for the first time. Subsequently these layers act as ionic conductors, and ideally they shall remain on the active mass unchanged during repeated charge/discharge cycles or in case of a primary battery during intermittent discharge. When left undisturbed growth of the layer will slow down with storage time and increasing film thickness, correspondingly self-discharge will decrease^[6]. Some of these layers have a rather high Ohmic resistance (e.g. those on lithium metal in contact with electrolyte solutions based on SO_2Cl_2 or SOCl_2 or SO_2 dissolved in acetonitrile) causing a voltage collapse when discharge is turned on: the voltage delay (Voltage delay means a temporary voltage decrease followed by a more or less quick restoration to the expected cell voltage^[6]). In particular when high discharge currents are drawn the SEI will crack and will be damaged more or less; in the previously addressed case the cell voltage will be restored. Thus it will be rebuilt when the load is disconnected, requiring further material from the cell inventory - more self-discharge. Self-discharge with different carbon materials has been compared at various temperatures^[47], higher self-discharge was found - as expected with respect to the discussion above - to be faster at elevated temperatures and with materials having a larger surface area. The rate of SEI formation - part of the self-discharge - was independent on carbon material at lower temperatures but differed significantly with material at elevated temperatures. Self-discharge of cells with SO_2Cl_2 is higher than with SOCl_2 ^[6].

In case of secondary batteries numerous cell designs and cell chemistries use host materials in the electrodes for metal (ion) insertion/deinsertion which may show volume and shape change during charge/discharge. This will negatively affect the deposited SEI/CEI-layers

by cracking and/or shedding and again initiate more layer formation with associated material consumption - causing self-discharge^[6].

In secondary batteries wherein SEI and/or CEI are found continuous self-discharge by reactions between the active masses and the electrolyte solution proceeds nevertheless because still some reaction between active mass and electrolyte solution happens, the same layers are relevant when being destroyed and reformed during charge/discharge. Although this is hardly the conventional type of self-discharge it has been included here because it can scarcely be separated and because the effect: loss of stored energy and cell inventory are the same.

Intrinsically conducting polymers like polyacetylene as active electrode materials may cause decomposition and thus self-discharge of organic solvent-based electrolyte solutions^[48]. In the latter case products of solvent composition further mediate and accelerate self-discharge of the *p*-doped (charged) polyacetylene. Further options like reaction of the *p*-doped polymer with impurities or intrinsic instabilities of the polymer have been considered^[48]. Quite differently polypyrrole was not found to "self-discharge" in its oxidized state when brought into contact with an electrolyte solution^[49]. Obviously its oxidizing capability was insufficient for any reaction with the electrolyte solution. Only in a complete cell, i.e. with the negative lithium electrode present, self-discharge was observed again. It was consequently attributed to some mobile and redox-active species generated by reaction of lithium with the electrolyte solution. Elsewhere a composite of polypyrrole and polyethylene oxide showed better performance than pyrrole alone in terms of storage capability but much poorer charge retention, i.e. higher self-discharge, for unknown reasons^[50]. By comparison lowest self-discharge was observed with polyaniline studied as a positive electrode, this was tentatively related to lower sensitivity of the polymer versus oxidation^[51].

Some electrode materials or reaction intermediates present only temporarily during electrode reactions show significant solubility and may thus diffuse to the other electrode and react directly with the active mass. This self-discharge is frequently encountered with secondary batteries employing sulfur as the positive electrode mass^[52]. The mechanism is commonly name

redox-shuttle mechanism, it causes self-discharge only during charging of the battery whereas further parasitic reactions of soluble polysulfides may affect the cell negatively at all times^[53,54]. A simplified reaction scheme is shown in **Figure 5**.

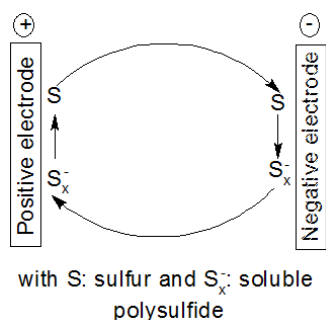


Figure 5. Scheme of a redox shuttle mechanism

Because sulfur itself shows only low solubility in most employed solvents instead of sulphur polysulfide anions with different states of oxidation may diffuse. This shuttle is still a major hurdle in development of Li-S-batteries which otherwise show very promising performance data, this mechanism will of course also show up with other negative electrode metals like calcium^[55]. There are numerous studies aiming at reducing this process^[53,56,57]. Basically this mode of self-discharge can be diminished by keeping the soluble intermediates in or close to the respective electrode or reducing the solubility of the intermediates in the used electrolyte solution.

Mixed conduction membranes have been suggested as another option to suppress the polysulfide shuttle^[58]. Among further possible remedies is physical confinement (trapping) of the elements as well as possibly mobile intermediates^[59]. In a similar approach multilayer encapsulation of sulfur has been proposed^[60], wrapping of sulfur particles in graphene is a further concept^[61], these approaches can be traced back to earlier and initial work aimed at better sulphur utilization and reduction of self-discharge^[62]. Adsorption (trapping) of polysulfides^[63], possibly combined with accelerated conversion of these species into less soluble ones has been studied^[64]. Catalytic options to meet the polysulfide shuttle challenge have been reviewed^[65,66]. Use of an interlayer (see also for another option of a functional interlayer^[67]) adsorbing polysulfides and accelerating their transformation into less detrimental species has been suggested^[68]. Further

similar approaches have been proposed elsewhere^[69,70], options to control polysulfide diffusion and thus reduce self-discharge have been compared^[71]. The influence of functional binders on self-discharge of Li/S-batteries has been addressed^[72]. Reviews of the polysulfide-related challenges in lithium-ion/sulphur batteries are available^[73,74], self-discharge has been stressed as a still significant bottleneck when comparing lithium-ion/sulphur batteries with other lithium-ion systems^[75]. Basically the same problems of increased self-discharge are found when substituting selenium for sulphur or using SeS_2 ^[59].

A similar shuttle mechanism as schematically depicted in **Figure 6** is found with the antipolar mass in nickel-cadmium electrodes^[6,10].

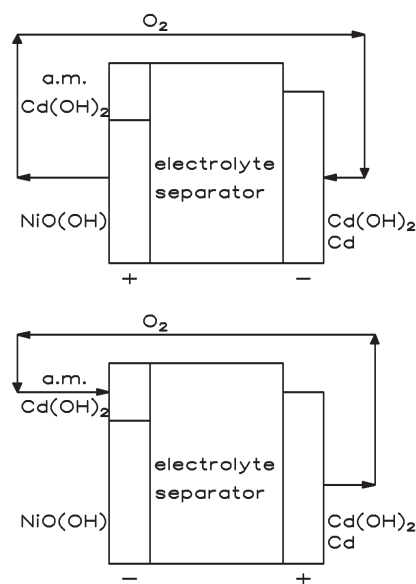


Figure 6. Antipolar mass a.m., scheme of its operation in a NiCd-accumulator on (top) overcharge, and (bottom) at deep discharge and polarity reversal, path of oxygen movement needed for pressure limitation indicated

The various shuttle processes are: Upon deep discharge of a NiCd-accumulator gas evolution might occur with associated problems of overpressure inside the cell. Because of production tolerances the actual capacity of cells might vary, thus in series arrangement single cells might undergo polarity reversal even though other cells are still properly discharged. This problem can be avoided by adding antipolar mass to one electrode. Commonly an amount of $Cd(OH)_2$ is added to the nickel electrode, the amount being large

enough that upon complete oxidation of cadmium in the negative electrode still unreduced $\text{Cd}(\text{OH})_2$ is present in the positive nickel electrode. Thus hydrogen evolution is inhibited. If partial pressure of oxygen developed at the negative electrode during overcharge by decomposition of water is large enough oxygen will be reduced at the cadmium of the antipolar mass. Because the mass of $\text{Cd}(\text{OH})_2$ is more than equivalent to that of $\text{NiO}(\text{OH})$ oxygen evolution will start first without associated hydrogen evolution. During normal operation self-discharge is not caused.

Adding redox mediators for improved performance of lithium-oxygen batteries causes the same redox-shuttle processes and associated self-discharge^[76], a Nafion[®]-based membrane separator with high lithium-ion selectivity is the obvious remedy: The use of non-carbon positive electrodes aiming at the reduction of unwanted side-reactions had resulted in significantly reduced discharge capacities. This could be remedied by adding two synergistic redox mediators for lithium peroxide formation and oxidation. Their cross-over to the negative electrode can be prevented with a suitable membrane. Broader perspectives of the problems associated with the use of redox-mediators acting as soluble catalysts for enhanced oxidation of Li_2O_2 during battery charging in lithium-oxygen batteries including self-discharge have been reviewed^[77].

Measurements of self-discharge currents of lithiated graphite during cycling map the complex ageing of this electrode^[78]. Among the various options to keep detrimental effects of overcharge of lithium-ion batteries small the addition of redox shuttles has been proposed^[79], quite obviously these additives may contribute to self-discharge according to the mechanism sketched above (**Figures 3 and 5**), in particular when their action becomes effective already at cell voltages and thus electrode potentials within the range of ordinary cell operation.

Utilization of the redox couple $\text{AlCl}_4^-/\text{Al}_2\text{Cl}_7^-$ as the negative half-cell of a battery has been hampered by its chemically aggressive behavior, in particular the lack of a suitable current collector^[80]. Addition of LiCl resulted in the formation of some coordination species inhibiting intercalation of the tetrachloroaluminate in the negative current collector; in addition this enables the use of established positive electrode materials from lithium-ion batteries resulting in a cell with minimal

self-discharge.

In high temperature liquid metal batteries with molten salts as electrolyte between the two molten metallic electrodes^[2,81] self-discharge is frequently caused by dissolution of an electrode metal in the molten electrolyte and subsequent movement of these species into the other electrode^[82,83]. Changing the composition of the molten electrolyte or the used metals or metal alloys has been reported as option^[82,83], using a solid ion conducting electrolyte instead of the molten electrolyte is a further possibility which unfortunately may cause new challenges regarding lower ionic conduction, wetting, costs and mechanical stability.

A general feature of high-temperature batteries^[84,85] is the need to maintain their operating temperature by heating when the battery stands idle and no Joule heating generated by the flow of current in the operating cell serves this purpose. The heat needed for this upkeep may be taken from the cell by e.g. running an electric heater from the cell, this amounts to (thermal) self-discharge. It can be reduced by better thermal insulation of the cells and battery modules.

6. Self-discharge in Redox Flow Batteries

In a redox flow battery (RFB) two half cells containing dissolved redox systems with different redox potentials combining into the cell voltage are connected via a suitable separator^[2,4]. Both solutions must be kept separate to avoid chemical reactions between the active ingredients resulting in discharge of the cell. In most device designs this separation is established by inserting a semipermeable ion-conducting membrane^[2,4]. Further options like porous separators for systems with larger redox ions are under consideration.

Self-discharge in RFBs can be caused by ion-crossover, i.e. unwanted mixing of redox components resulting in direct chemical reactions and undesired heating of the cell. Further processes causing self-discharge are chemical reactions between redox constituents and cell components, i.e. oxidation of electrode materials by highly oxidizing compounds in the positive electrode half-cell. Because the electrolyte solutions in the half-cells will be circulated by external pumps (in case of hybrid systems where a solid electrolyte is combined with redox-half-cell there may be one pump only) running the pumps even when the RFB is in idle condition will cause energy

consumption, energy is drained from the amount stored in the device. This will also finally result in “self-discharge”. Further auxiliary devices needed to monitor and control proper operation of the RFB will also cause energy consumption. Similar to devices monitoring the state of a battery module or a battery pack this will also result in consumption of electrical energy most likely drained in all cases from the energy initially stored in the device.

Self-discharge caused by ion crossover is closely related to imperfections of the used separator, whether it is a semipermeable membrane or a highly porous material. In case of e.g. an all-vanadium RFB the membrane should completely prohibit transport of vanadium species and water but permit transport of other charge carrying species involved in charge balancing like H^+ , SO_4^{2-} , and HSO_4^- . A perfect membrane does not exist; consequently researchers have tried to identify most suitable membranes and have tried to improve their properties (perm selectivity, Ohmic resistance, chemical and mechanical stability). Because the currently most frequently used membranes based on perfluorosulfonated or -carboxylated PTFE tend to be expensive price considerations, i.e. getting cheaper membranes, add a further dimension to the engineering and chemical challenges^[86]. Improved permselectivity of a Nafion[®]-based membrane (and thus lower self-discharge) can be afforded by incorporating inorganic nanoparticles^[87-89] and by further modifications of the membrane^[4,90]; this includes application of additional barrier layers^[91] and double layer membranes^[92]. Use of an anion exchange membrane containing silica nanoparticles has been suggested as a further option reducing self-discharge by ion crossover and also reducing costs^[93]. Modeling of self-discharge of an all-vanadium RFB assuming a diffusion rate of vanadium ions depending on diffusion coefficient, partition coefficient and concentration gradient was found to provide a good description of the experimentally observed changes^[94]. A further modeling approach taking into account further experimental data as well as other processes contributing to self-discharge has been developed aiming at its inclusion in the cell control software with particular regard to the need of cell rebalancing^[95]. In a theoretical study of self-discharge-related reactions in an all-vanadium RFB polymerization reactions of

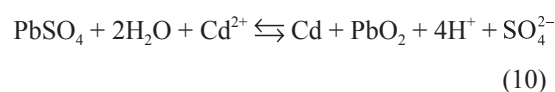
vanadium ions and participation of multivalent ions have been highlighted^[96].

A further option to reduce ion crossover is the use of redox-active electrolyte components large enough in the solvated state to slow down or even inhibit passage through the membrane. Numerous materials have been proposed, polyoxometalates^[97] are among them. Self-discharge by ion crossover has also been observed when using a cerium-based half-cell^[98].

Oxidation of cations in the negative half-cell of e.g. an all-vanadium RFB by dioxygen from ambient air in an essentially open system may also result in self-discharge^[99]. The suggested remedies are obvious: Smaller surface area of the electrolyte solution reservoir exposed to air is obvious, higher electrolyte concentrations apparently also slows down oxidation of V(II) by dioxygen.

In practical setups frequently several RFBs are connected in series. Distribution of the electrolyte solution with manifolds *etc.* results in shunt currents, this in turn causes self-discharge. It has been modeled^[100]. Growing self-discharge with increasing number of connected cells does not come as a surprise because the larger overall voltage drop provides a higher driving force. An extensive study of a practical 200 kW/400 kWh all-vanadium RFB has been reported^[101]. Up to 24% of the delivered energy was consumed by peripherals necessary to operate the RFB, separate numbers directly indicative of self-discharge were not provided. When the RFB was kept in an operational state needed for fast response (spinning reserve, primary operating reserve) up to 80% of the charge were lost in 48 h.

In addition to the prototypical RFB with two circulated liquid electrolyte solutions with a membrane or another separating item other electrode combinations have been proposed^[2,4]. Among them is the combination of a solid metal negative electrode with a second half cell with a circulated dissolved electrolyte, another one is the use of two solid electrodes with an electrolyte solution as suggested in^[102] with a negative cadmium and a positive lead dioxide electrode. The cell reaction is



with an aqueous electrolyte solution of 1 M $CdSO_4$ and 2 M H_2SO_4 . Self-discharge is caused by reduction

of water by the cadmium electrode thermodynamically unstable in this electrolyte solution with associated hydrogen evolution. The rather high overpotential of the hydrogen evolution reaction at the cadmium electrode already limits self-discharge, electrolyte solution additives (DPE-3) have been suggested for further inhibition^[102]. A similar design with a negative zinc electrode faced even more serious self-discharge by hydrogen evolution at the negative electrode^[103].

Half-way between the two cell principles addressed above are RFBs with a solid electrode combined with another half-cell containing a redox system. The zinc/bromine or zinc/iodine systems are typical examples. Self-discharge in these cells proceeds by formation of local elements (**Figure 4b**) on the negative zinc electrode involving dissolved impurities deposited on the zinc surface and chemical reactions between the halogen and zinc possible when the separator does not work perfectly^[104].

7. Remedies: Ways to Limit Self-discharge

Numerous approaches to limit or slow-down self-discharge have already been addressed above when presenting examples. Because electrode reactions are by definition heterogeneous processes at the electrode/electrolyte interface researchers have tried to make this interface as large as possible. Because most self-discharge reactions are also heterogeneous processes any increase of surface area will help both the wanted and the unwanted electrode reactions. When having achieved an optimized electrode morphology in terms of surface area and porosity this should not change too much during charge/discharge (e.g. by disintegration of active mass particles caused by volume expansion or pulverization initiated otherwise) because this will also enhance self-discharge, in addition it might consume active material during formation of surface layers.

Additives in the electrolyte solution have been applied with both aqueous and non-aqueous electrolyte solutions. Their task varies from inhibition of parasitic electrode reactions (“corrosion”) to binding unwanted and detrimental impurities introduced via the electrodes and/or the electrolyte solution to catalyzing processes participating in the removal of unwanted species. The case of lithium batteries has been reviewed by Zhang *et al.*^[105].

Taking a broader perspective of self-discharge including energy consumed by peripheral devices

(keeping in mind that there appears to be no well-defined boundary between essential components of a battery and a peripheral device) the obvious contribution to reduced self-discharge from these components can be obtained by selecting energy-efficient pumps in an RFB, using electronic circuitry for control and monitoring with lowest possible energy consumption and switching off devices whenever possible.

Avoiding overcharge of a battery of all types seems to be an option both simple and effective to maintain battery health and reduce subsequent self-discharge.

8. Conclusions

Self-discharge of batteries is a natural phenomenon driven by the same forces which enable use of a battery during discharge. Numerous processes mostly at the electrode interface in terms of chemical reactions between active masses, auxiliary materials and electrolyte (solutions) are responsible, in addition in some cases shuttle processes across the ionically conducting phase between the electrodes contribute to self-discharge. Understanding the ongoing processes has already resulted in numerous suggestions to remedy self-discharge, deeper understanding and further study will result in more options and remedies. More careful consideration of possible side-reactions and effects of impurities in all constituent materials have enabled significant progress towards devices with lower self-discharge.

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