

Chloride Ion Battery Review: Theoretical Calculations, State of the Art, Safety, Toxicity and an outlook towards future developments

Gschwind, F.; Euchner, H.; Rodriguez-Garcia, G.;

Originally published:

June 2017

European Journal of Inorganic Chemistry 2017(2017)21, 2784-2799

DOI: <https://doi.org/10.1002/ejic.201700288>

Perma-Link to Publication Repository of HZDR:

<https://www.hzdr.de/publications/Publ-25272>

Release of the secondary publication
on the basis of the German Copyright Law § 38 Section 4.

Chloride Ion Battery Review: theoretical calculations, state of the art, safety, toxicity and an outlook towards future developments

F. Gschwind^{a*}, Holger Euchner^a, and Gonzalo Rodriguez-Garcia^b

^aHelmholtz Institute Ulm (HIU), Helmholtzstrasse 11, 89081 Ulm, Germany

^bInstitute of Fluid Dynamics, Helmholtz-Zentrum Dresden-Rossendorf (HZDR), Bautzner Landstrasse 400, 01328

Abstract

Batteries using chloride ions as shuttles have only been under investigation for a few years, but already several publications have dealt with this topic. In this review, we extensively report for the first time the state of the art, as well as research on chloride ion batteries and chloride conduction. Moreover we present a theoretical screening along with calculations of the capacities and volumetric and gravimetric densities. We also present theoretical calculations of the capacities and volumetric and gravimetric energy densities as well as an analysis of safety and toxicity. At the end, possible future approaches are evaluated.

1. Introduction

Electrochemical storage has become an integral part of our daily lives. From large stationary batteries to small portable gadgets, the ability to store electrical energy is of utmost importance for modern society.

Currently, the best-performing battery systems are based on cation shuttles. Especially, Li-ion batteries (LIBs) can provide high-voltage, lightweight storage systems. Other cations systems have also been investigated such as Na⁺, Ca²⁺, and Mg²⁺ [1] [2] [3] [4] [5] [6] [7].

As the anion, the best-known species is OH⁻, which is found in the well-known alkaline batteries or nickel–metal hydride system. Fluoride ion batteries [8] [9] [10] [11] [12] [13] [14] [15] [16] and to some extent aluminum batteries, which use “AlCl₄⁻” shuttles, [17] [18] offer other alternative anions.

After fluorine, chlorine is the second most electronegative element in the periodic table and is therefore very stable as an anion, with a large electrochemical stability window. Like fluoride ions, chloride ions can also be regarded as suitable for charge transfer in a battery. The transfer of chloride ions between the electrodes could reversibly store electrons by charge compensation in the electrochemical couple. The theoretical working principle of chloride ion batteries (CIBs) is illustrated in Figure 1.

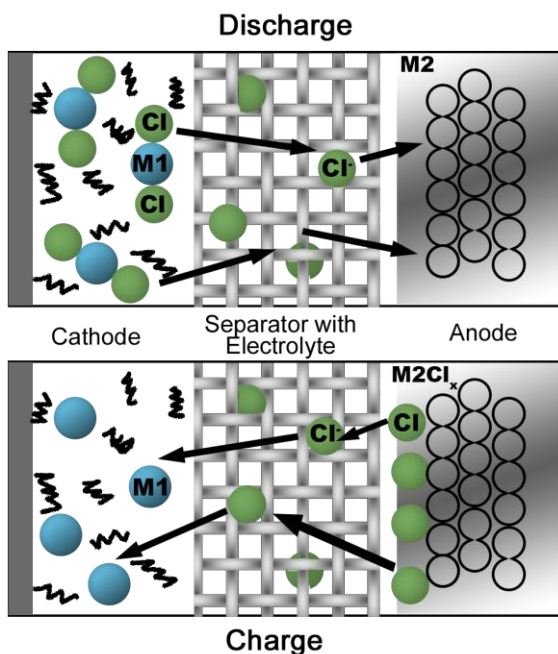


Figure 1: Working Principle of the general discharge and charge processes of a CIB

During the discharge process, the anode materials oxidize and release electrons into the electric circuit. These electrons reduce the chloride salt, which acts as the cathode material. Charge neutrality is maintained by the transport of chloride ions through the electrolyte.

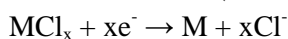
Bivalent or trivalent salts are especially interesting as cathode materials since they release more than one electron per metal atom and therefore lead to a higher gravimetric density than monovalent salts. Metal chloride with various weights can also achieve desirable volumetric energy densities.

While CIBs will not achieve the high capacities or voltages of LIBs, which are currently the best-performing batteries, they remain nevertheless attractive because of chloride materials being widely available.

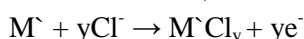
2. Theoretical Calculations and Screening

The performance of any battery is determined by the electrochemical reactions occurring at anode and cathode, respectively. In a CIB, these reactions in their most general appearance can be expressed as follows:

Cathode reaction (reduction):



Anode reaction (oxidation):



While it is common to quantify Li ion batteries with respect to capacity and energy density of the cathode material by assuming Li metal as anode, in case of CIBs (and other batteries based on conversion reactions) so far no obvious standard anode/cathode material is available. Therefore, to judge the properties of a CIB it is necessary to account for both half cell reactions. Now, this obviously leaves us with a huge

number of possible anode/cathode combinations. In the following, we have conducted a screening for a large number of such combinations to be able to rate them with respect to capacity and energy density.

This screening is based on experimental data (enthalpy of formation and unit cell volume) that have been extracted from the materials project database ^[19a] by making use of the PymatGen package ^[19b]. The resulting values are, however, theoretical predictions of the pure material combinations and do not take into account the impact of other components that are essential for a functioning battery system such as electrolyte, separator or binder.

The open circuit voltage (OCV) of a CIB can be obtained from the difference in Gibb's free energy (chlorine chemical potential) of anode and cathode material. Disregarding entropic contributions, the OCV of a given anode/cathode combination can thus be expressed via the extracted formation enthalpies ΔH_f of the respective compounds by applying the following formula:

$$OCV(MCl_x, M'Cl_y) = \frac{\frac{1}{x}\Delta H_f(MCl_x) - \frac{1}{y}\Delta H_f(M'Cl_y)}{-e}$$

Here, $-e$ denotes the elementary charge of an electron, while the prefactors $1/x$ and $1/y$ are introduced to normalize the reaction to the transfer of one chloride ion. The OCVs that are calculated according to the above equation correspond to the average voltage of the investigated combination, as they are obtained only from initial and final configuration. This means that no information on underlying reaction pathway and discharge profile, which may proceed via metastable intermediates, can be extracted.

The determination of the gravimetric capacity of the corresponding anode/cathode combination c_m can easily be conducted by considering the minimum mass that is needed for the storage of one chloride ion:

$$m_{ges} = \frac{1}{x}m(M) + \frac{1}{y}m(M') + m(Cl)$$

Consequently, the gravimetric capacity is then obtained by dividing the transferable charge per chloride ion by the total mass necessary for storing the latter one:

$$c_m(MCl_x, M'Cl_y) = \frac{-e}{m_{ges}}$$

Similarly, the volumetric capacity c_v of such a system can be estimated. Assuming that the volume of the respective phases $V(MCl_x)$ and $V(M'Cl_y)$ is larger than the volume of the corresponding metals, we can define an upper limit of the required storage volume:

$$V_{ges} = \frac{1}{x}V(MCl_x) + \frac{1}{y}V(M'Cl_y)$$

Accordingly, the lower boundary of the volumetric capacity can be expressed as:

$$c_v(MCl_x, M'Cl_y) = \frac{-e}{V_{ges}}$$

The respective capacities c_v and c_m directly allow us to determine the corresponding gravimetric and volumetric energy densities ρ_m and ρ_v :

$$\rho_{m/V} = OCV(MCl_x, M'Cl_y) * c_{m/V}(MCl_x, M'Cl_y)$$

In practice, we have selected 50 potentially suitable MCl_x compounds and by making use of the above expressions, we have investigated all resulting 1225 anode/cathode combinations $MCl_x / M'Cl_y$ for gravimetric capacity and volumetric energy density (see Fig. 2).

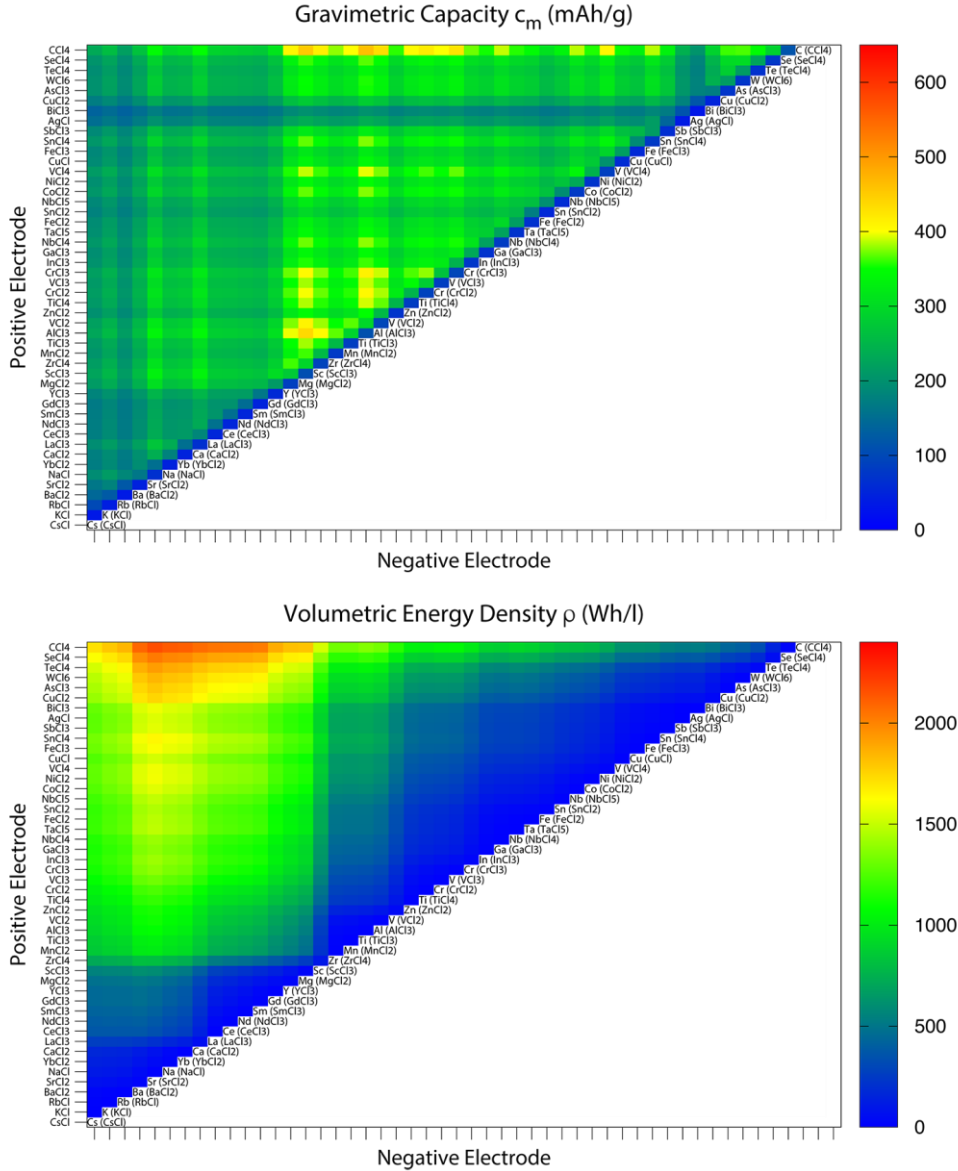


Figure 2: Overview of gravimetric capacities and volumetric energy density of different combinations of $MCl_x / M'Cl_y$, blue colors show the lowest values while yellow and red are attributed to the best performers.

When regarding the volumetric energy density ρ_V plot in Fig. 2, it can be inferred that several anode/cathode combinations (altogether 18) reach values beyond 2000 Wh/l which is almost twice the value of a Li-ion battery (1015 Wh/l) and brings them close to the 2199 Wh/l of Li-S batteries^[8]. Similarly, 26 combinations show a gravimetric energy density ρ_m beyond 1000 Wh/kg which is to be compared to 387 Wh/kg of Li-ion batteries^[8]. For the gravimetric capacity c_m on the other hand, we find a large number of combinations with values above 400 mAh/g, meaning that Li-ion batteries are again clearly outperformed by chloride ion

batteries. In Table 1 we retrieved from the calculated data the top 20 combinations from our calculated data to investigate how realistic they would be in a real battery.

Table 1: Cell combinations yielding the 20 highest theoretical capacities and volumetric and gravimetric energy densities. “+” denotes the cathode, while “-” denotes the anode.

+	-	mAh/g	+	-	Wh/L	+	-	Wh/kg
CCl₄	Al	564	SeCl ₄	Sr	2219	CCl ₄	Ca	1728
CCl₄	Ti	531	CCl ₄	Sr	2189	CCl ₄	Na	1706
CCl₄	Mg	529	SeCl ₄	Yb	2146	CCl ₄	Mg	1574
CCl₄	V	523	SeCl ₄	Na	2130	CCl ₄	K	1442
CCl₄	Sc	501	CCl ₄	Yb	2120	CCl ₄	Sc	1415
CCl₄	Ti	492	SeCl ₄	Ca	2106	SeCl ₄	Ca	1294
CCl₄	V	483	CCl ₄	Na	2105	SeCl ₄	Na	1293
CCl₄	Cr	480	CCl ₄	Ca	2082	CCl ₄	Sr	1285
TiCl₄	Al	475	SeCl ₄	La	2060	CCl ₄	Y	1221
AlCl₃	Mg	473	SeCl ₄	Ce	2056	CCl ₄	Al	1178
CCl₄	Nb	469	SeCl ₄	Nd	2049	SeCl ₄	K	1147
CCl₄	Fe	469	SeCl ₄	Sm	2049	SeCl ₄	Mg	1128
VCl₄	Al	468	CCl ₄	La	2036	CCl ₄	La	1058
CCl₄	Se	460	CCl ₄	Ce	2032	CCl ₄	Ti	1055
CCl₄	Ca	458	CCl ₄	Nd	2025	VCl ₄	Na	1049
AlCl₃	Sc	450	CCl ₄	Sm	2024	CCl ₄	Ce	1040
TiCl₄	Mg	449	SeCl ₄	Gd	2016	VCl ₄	Ca	1039
MgCl₂	Mg	448	WCl ₆	Sr	2002	SeCl ₄	Sr	1030
VCl₄	Ti	445	CCl ₄	Gd	1993	SeCl ₄	Sc	1025
VCl₄	Mg	444	SeCl ₄	Ba	1983	CCl ₄	Ba	1025

Throughout the table, the best combinations are clearly based on carbon tetrachloride (CCl₄) as the cathode. CCl₄ is a toxic, carcinogenic liquid, with a melting point of -23°C and a boiling point of 76°C. It reacts violently with aluminum and alkaline metals and can form phosgene with humidity. Overall, it is not a very reasonable or practical option as a battery cathode. In addition, the reduction of all four chlorines to yield pure carbon is unlikely. After CCl₄, titanium tetrachloride (TiCl₄) and aluminum trichloride (AlCl₃) is one of the best combinations. Large quantities of TiCl₄ are used to produce titanium metal (Kroll Process), and it is liquid at room temperature. However, it is also toxic and reacts with humidity. A possible reduction to a lower valence might be possible, and battery configurations with liquid cathodes (such as thionylchloride batteries) exist. Therefore, developing this cathode material as well as the liquid VCl₄ is a potential area of future research. Furthermore, the table indicates that Sr is a good choice of anode. However, this is also a very unrealistic option for batteries due to its high reactivity. Selenium tetrachloride (SeCl₄) is also toxic and highly reactive, but in combination with Na, i.e., SeCl₄-Na (2130 Wh/L), it could be investigated as there is no obvious reason to discard this combination. As a cathode material, the most stable option on this list would be AlCl₃.

These considerations are purely theoretical, however, and the following state of the art section will show that CIBs are still at the initial stages of research. It will take a long time to reach the theoretical values listed in this table.

3. State of the Art

Good chloride transport throughout the battery (electrodes and electrolyte) and electrical conductivity in the electrode material are fundamental for CIBs, especially since chloride salts are generally insulators.

Therefore, we will first start with a short review of chloride conductors (CCs) in general.

3.1 Chloride Ion Conductors (CC)

Among solid-state CCs, PbCl_2 was the first investigated compound ^[20]. The chloride conduction is due to Schottky defects and anion vacancy sites. More chloride salts were determined to be chloride conductive such as CsPbCl_3 ^[21], SrCl_2 ^[22] and BaCl_2 ^[23], but these salts are conductive at quite high temperatures and are therefore out of the scope of this review.

Okamoto et al. further investigated CCs, and they proposed calcium-doped lanthanum oxychloride ^[24], which exhibits a conductivity of 7.1×10^{-4} S/cm at 700°C. These oxychloride compounds can be easily prepared and are also stable in water ^[25]. A very detailed report by Murin et al. reviews the progress in chloride solid electrolytes and provides further insights into the high conductivities of PbCl_2 and SnCl_2 ^[26]. They doped these salts with KCl, NaCl, or RbCl, which have similar cationic radii, in order to increase the amount of defects in the lattice.

For use in all-day energy storage, however, conduction at temperatures above 150°C are too high. While there might be applications where high temperatures are required, this is not in the scope of this review. We therefore gathered the available data from the literature for conductivity at 150°C, which is a reasonable temperature for halogenide conducting batteries ^{[16] [12] [27] [28] [10]}. The data are given along with the corresponding references in Table 2.

Table 2: Conductivity of different chloride compounds

Compound	Temp (°C)	Conductivity (approx) (S/cm)	Reference
undoped PbCl_2	150	10^{-1}	20
$\text{PbCl}_2/\text{KCl}_2$	150	10^{-3}	26
CsPbCl_3	150	10^{-5}	21
SnCl_2 (single crystal)	150	10^{-4}	26
BaCl_2	150	10^{-8}	26
LiCl crown ether	25	10^{-4}	29
Cryptand NaCl	100	10^{-5}	31
PolyDADMAC	150	10^{-2}	33

*= polydiallyldimethylammonium chloride

In addition, solid inorganic compounds, complexes and coordination compounds were also investigated. Newman et al. were the first to propose halogenide conduction in crown ether complexes ^[29]. The conductivity of LiCl with dibenzo-18-crown-6-ether was measured to be 4.4×10^{-4} S/cm at 25°C with a very low electronic conduction (0.001%). The transference number determined by Tuband's electrolysis method was found to be nearly 1. The good transport of chloride ions was attributed to the reduced Coulomb attraction between the ions and the absence of an insulating phase, since the complex could be obtained in its

pure form. Highly effective lattice disorder due to the solidification of the crown ether molecules in different conformations enable chloride ions to move easily along these defects ^[30].

In addition, cryptands were tested for halogenide conductivity, and iodide-containing complexes were found to exhibit much higher conductivity than crown ether complexes ^[31], even though the chloride contents appeared similar. These results were attributed to even lower Coulomb attractions between the metal cation and halide ion.

Polymer electrolytes can also be used for CCs. However, there are only a few studies in the literature dedicated to chloride transport through polymer electrolytes, as most research on polymer electrolytes has focused on alkaline ions. Nevertheless, cation-conducting polymers such as polymer electrolytes are well known to be able to conduct anions as well, thus contributing to the total ionic conductivity ^{[32] [33] [34] [35]}. Anchoring the cation onto a positively charged backbone is a promising strategy for polymer CCs, as proposed by Hardy et al. ^[33] using polydiallyldimethylammonium chloride (PolyDADMAC). Interestingly, the quaternary nitrogen on the polydimethylammonium backbone is surrounded by four alkyl groups, thus affording charge separation and decreasing the tight ion pairing. Polydimethylammonium chloride plasticized with tetraethylene glycol showed a conductivity of about 10^{-5} S/cm at 150 C° (at the best polydimethylammonium chloride to tetraethylene glycol ratio).

Further, CC membranes designed specifically for CIBs ^[36] will be discussed in the next section. For sensing applications, chloride-transporting smart membranes ^{[37] [38]} and ionophores, i.e., special carrier molecules, have also been reported ^{[39] [40] [41]}

Other investigations into chloride migration were performed in different biological studies such as chloride transport through special channels in and out of cells ^[38] and biological tissue ^{[42] [43] [44]}. Anion-exchange membranes that exchange halogenides can also be used to understand transport mechanisms for chloride ^{[45] [46]}.

Meanwhile, chloride transport has been widely investigated in research on concrete, especially for the marine environment ^{[47] [48] [49]}, where the diffusion of chloride has a major impact on the durability of concrete. However, this transport is only based on diffusion and is not influenced by the application of electrical fields, in contrast with battery systems.

3.2 Chloride Ion Batteries: General discussion

The following table (Table 3) provides an overview of the existing literature on CIBs:

Table 3: Known literature on CIBs

reference	cathode	Anode	Electrolyte	Best observed cycling	Best observed capacity (first discharge, mAh/g)	Estimated nominal voltage (V)	OCV (V)	Discussed problems
50	CoCl ₂ VCl ₃ BiCl ₃	Li	OMIMCl BMIMBF ₄	3	140	2.4	3.3	Dissolution of cathode material
51	FeOCl BiOCl	Li	N ₁₁₆₍₁₄₎ Cl N1114 TFSI	6	60	2.2	2.8	Postulated transformation BiOCl to Bi-oxide was not clearly observed
64	FeOCl BiOCl	Mg	PP14Cl PP15 TFSI	30	125	1	2.4	Formation of a MgCl ₂ passivation layer

52	VOCl	Mg MgCl ₂	PP14Cl PP15 TFSI	50	80	1-1.2	2.4	No clear evidence of VO
53	VOCl	Li	PP14Cl in PC	50	150	1.6	2.8	Possible intercalation of cations in VOCl
59	PPy on CNT	Li	PP14Cl PP15 TFSI	40	118	2.2	3.7	Using polymer as a cathode
36	BiCl ₃ PANI	Zn	TBACl in Gelatine, PVDF-HF PVC	-	150	0.8	1.2	Very rudimental battery set up, built in air. Only discharge tests

A few general remarks are appropriate before we discuss the state of the art in more detail. As shown in Table 3, until now, metal chloride salts and oxychloride metal salts were mostly used as a cathode material with traditional anode materials such as Li, Mg, and Zn. Most studies used ionic liquids as the electrolyte, but some reports proposed polymer electrolytes. The table shows the best capacity value from each publication, but these values differ widely depending on the current used. For the nominal voltage, we attempted to obtain an "average" nominal voltage by visually inspecting the discharge curves. However, this is insufficiently quantitative, and we therefore present a selection of discharge curves in [Figure 3](#).

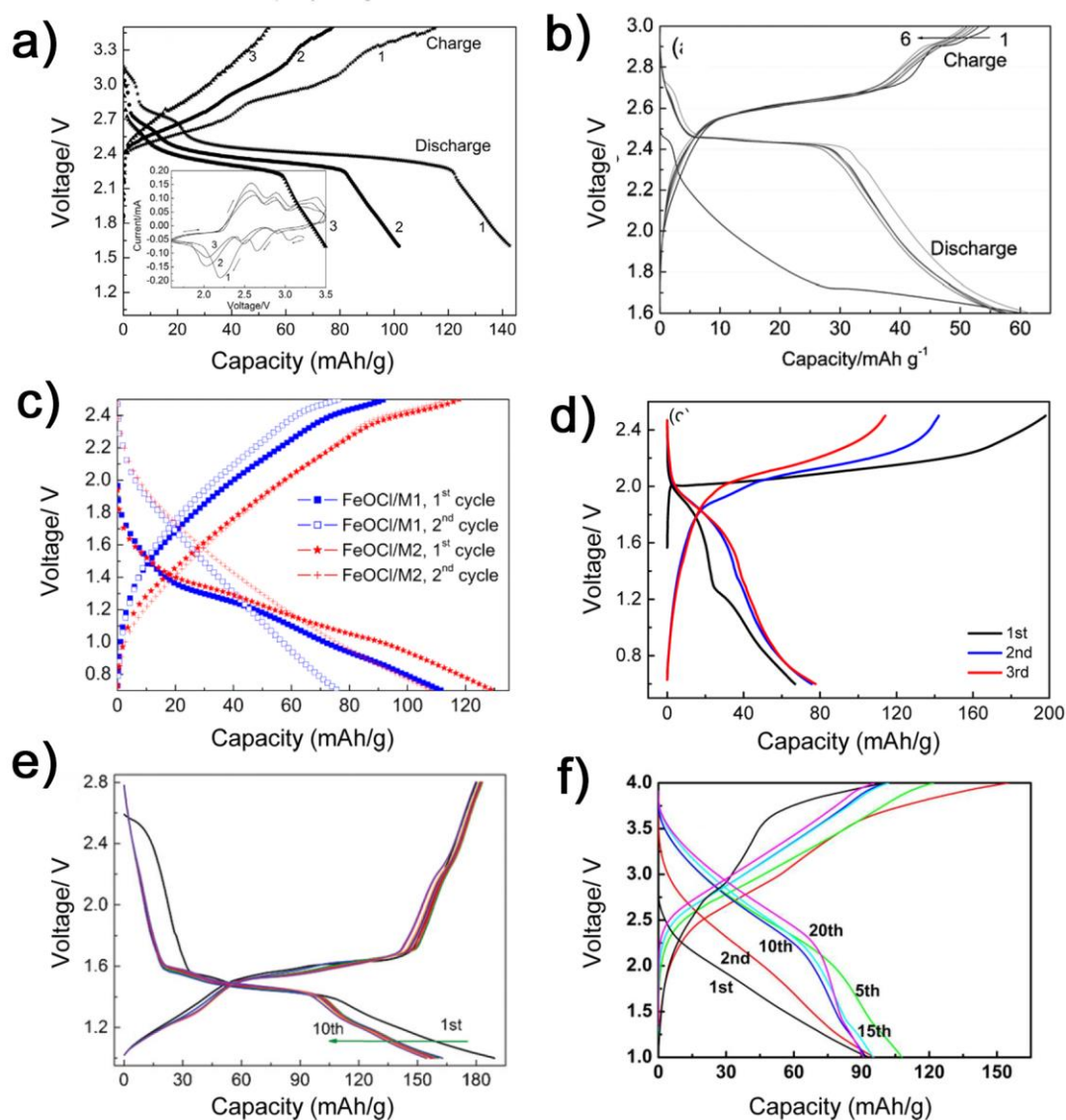


Figure 3: Various discharge curves from the publications of Zhao et al. and Gao et al. ^[50-53, 59, 64]. a) Three cycles of the cell BiCl_3 vs. Li. b) Six cycles from the cell with BiOCl vs. Li. c) First two cycles of a cell with FeOCl vs. Li. d) Three cycles of a cell with VOCl as the cathode and a mix of Mg/MgCl_2 as the anode. e) First ten cycles of a cell with VOCl as the cathode but with Li as the anode. f) A new type of cell with an organic-based cathode (polypyrrole on carbon nanotubes) vs. Li.

The various discharge curves exhibit significant differences. Some have very steep slopes, while others exhibit a distinct plateau. Chemically similar systems such as BiOCl (b) and VOCl (e) have very similar curves, thus suggesting that the underlying mechanism could be similar. All these details are discussed in the next sections.

3.3 First Proof of Principal

The principle of a chloride ion battery is based on a conversion mechanism, wherein metal chloride salts are transformed to the elemental form and vice versa (see Figure 1).

The first proof of principle was proposed by Zhao et al. ^[50] As the electrolyte, a mixture of ionic liquids (1-methyl-3-octylimidazolium chloride (OMIMCl) and 1-butyl-3-methylimidazolium tetrafluoroborate,

(BMIMBF₄) was used. In the authors' first paper, three simple chloride salts, namely, CoCl₂, VCl₃, and BiCl₃, were mixed with carbon black (20 wt%) and used as the cathode, while the anode was Li. The systems were cycled between 3.5 V and 1.6 V.

In the CoCl₂ system, the best-performing discharge was reported for an ionic liquid (IL) mixture with an IL containing four times more non-chloride ions as OMIMCl. The best capacity was 105.2 mAh/g (theoretical 412.8 mAh/g), which is attributed to the solubility of CoCl₂ in the electrolyte. However, no picture or description indicated whether the electrolyte changed color due to cobalt dissolution. Li⁺ could also dissolve in the electrolyte, but in that article, the electrolyte was not further analyzed. Nevertheless, the X-ray diffraction analysis (XRD) pattern after discharge showed the presence of metallic Co on the cathode side and the presence of LiCl on the anode side, giving some indication that the stated mechanism took place.

In addition, the BiCl₃ cathode also demonstrated good performance, exhibiting an open circuit voltage (OCV) about 0.3 V higher than the calculated one, and a discharge capacity of 140 mAh/g (first discharge) could be obtained over three cycles. Unfortunately, the capacity faded to half its initial value after these three cycles. The presence of metallic Bi could be proven by XRD, which provided evidence for the proposed conversion mechanism.

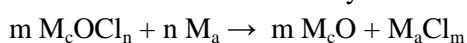
Moreover, the VCl₃ systems demonstrated an interesting OCV of 3.3 V (theoretical 2.21 V mentioned in the report of Zhao et al.). However, this observed overpotential was not explained in the article. After discharge, the VCl₃ system exhibited a complete loss of the crystalline peaks in XRD, which suggests that the crystal structure was completely lost.

In conclusion, the first challenge of CIBs is the dissolution of the cathode active material into the electrolyte. This paper also draws attention to another problem, i.e., the large volume change that accompanies the transformation of metals to metal chlorides and vice versa. These changes could lead to the disruption of the conductivity path and lower the battery performance.

3.4 Cathode Development

To prevent the dissolution of the cathode material, new cathodes have been proposed based on metal oxychloride salts^[51], which are more stable because the metal cations are bonded to the strong Lewis basic O²⁻ anion. These chloride compounds form adjacent layers that are held together by van der Waals interactions^[51].

The overall reaction of this system is:



A BiOCl/Li system allow for six cycles with a capacity of 80 mAh/g and a discharge plateau of about 2.4 V. Two different electrolytes systems were tested: butyltrimethylammonium chloride (N₁₁₆₍₁₄₎Cl) in butyltrimethylammonium bis(trifluoromethylsulfonyl)imide (N₁₁₄TFSI) and 1-butyl-1-methylpiperidinium chloride (PP₁₄Cl) in 1-butyl-1-methylpiperidinium bis(trifluoromethylsulfonyl) imide (PP₁₄TFSI). The reduction of the BiOCl phase was investigated in detail. BiO is unstable and should decompose into Bi and Bi₂O₃. While the presence of metallic Bi was proven, the Bi₂O₃ phase could not be found (Figure 4a, second line). This is not surprising, however; Bi halogenide salts (BiX₃) are widely used in halogenide batteries precisely because of this easy reduction to metallic Bi, which is easy to detect by XRD^[36]. Interestingly, in the as-prepared powder, peaks indicating metallic Bi seemed to appear in the XRD pattern (Figure 4a, first line). The reversible oxidation reaction was also confirmed, and in the charged electrode, the intensity of the Bi metal peaks drastically decreased (Figure 4a, last line).

Figure 4: XRD pattern after discharge of BiOCl (a) and of FeOCl (b). Taken from the publication^[51]. Bi=*

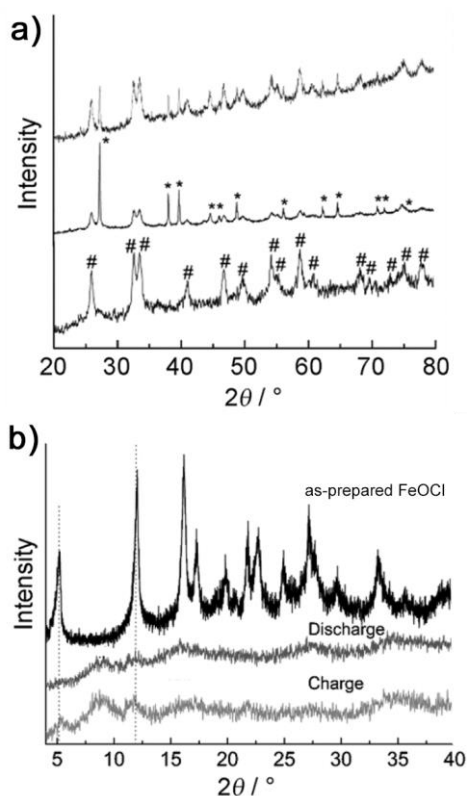


Figure 4: XRD pattern after discharge of BiOCl (a) and of FeOCl (b). Taken from the publication ^[51]. *=Bi

Furthermore, FeOCl was tested against Li as the anode (Figure 4b). The cycling behavior of this system was far better than in the BiOCl system, and 25 cycles could easily be performed. However, no diffraction peaks were observed indicating a possible wüstite FeO phase. The authors suggested that this phase might be nanocrystalline or amorphous and was therefore not detectable by XRD. However, high-resolution transition electron microscopy (HRTEM) suggested the presence of Fe₃O₄, and it was proposed that the magnetite formed upon the oxidation of wüstite. A scanning transmission electron microscopy (STEM) analysis demonstrated distinct morphology changes before and after cycling and thus could confirm this thesis; nonetheless, the evidence was scarce.

Further cathode reports also proposed the use of VOCl ^[52] ^[53], which performed very well in a series of different battery systems such as in the widely used LIBs ^[54] ^[55] ^[56], sodium ion batteries ^[57] and Mg ion batteries ^[58]. VOCl seems to have a wide range of electrochemical behaviors depending on the anode used, and the following mechanisms have been proposed for the different systems (Table 4).

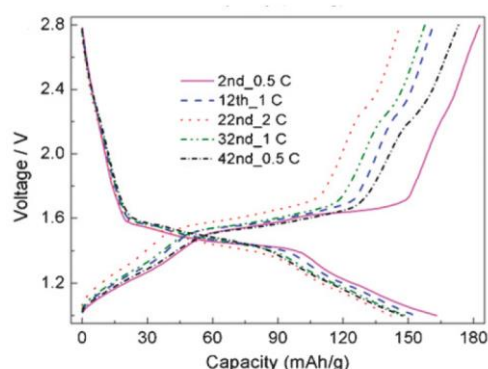
Table 4: Mechanisms proposed for VOCl as cathode material

Battery System	Proposed mechanism by the authors
VOCl - Li (Cl-electrolyte)	$\text{VOCl} + \text{Li} \rightarrow \text{VO} + \text{LiCl}$ (based on information in literature)
VOCl - Mg/MgCl ₂ (Cl-electrolyte)	first charge: $2\text{VOCl} + \text{MgCl}_2 \rightarrow 2\text{VOCl}_2 + \text{Mg}$ discharge process: $2\text{VOCl}_2 + \text{Mg} \rightarrow 2\text{VOCl} + \text{MgCl}_2$ $2\text{VOCl} + \text{Mg} \rightarrow 2\text{VO} + \text{MgCl}_2$
Reference battery: VOCl - Li (Li-electrolyte)	$\text{VOCl} + 3\text{Li}^+ + 3\text{e}^- \leftrightarrow \text{Li}_2\text{O} + \text{V} + \text{LiCl}$

The VOCl-CIBs operated with 0.5 M PP₁₄Cl in propylene carbonate as the electrolyte. The electron conductor was carbon black.

In the report on VOCl vs. Li^[53] the discharge curves were described as follows: a first plateau at 2.5 V corresponds to 0.07 mol electron transfer and is attributed to the intercalation of the electrolyte cation in the VOCl structure as reported in other articles cited by the author. The plateau at 1.6 V is not further commented, but could maybe be associated with loss of chloride ions. The mechanism was investigated using XRD, STEM, X-ray photospectroscopy (XPS), and HRTEM. The evolution of trivalent vanadium to bivalent vanadium could be observed during discharge. Furthermore, infrared spectroscopy (IR) of the cathode also showed organic signatures, revealing the presence of electrolyte in the pores. In conclusion, all analyses indicated an irreversible intercalation of the IL cation in the VOCl structure along with intercalation of chloride. This structural change facilitates chloride intercalation, which seems to be the reason for the good reversibility of the capacity even at high current densities. (Figure 5)

Figure 5: Cycling performance of the VOCl vs. Li cell at different C-rates. Taken from publication^[53]



The possible dissolution of LiCl/Li⁺ into the electrolyte along with the subsequent intercalation cannot be neglected. Investigation of the electrolyte is therefore necessary to yield new insights. The different mechanism of VOCl against a half-charged Mg/MgCl₂ anode will be further discussed in the section "Anode."

Zhao et al. ^[59] and Gschwind et al. ^[36] both proposed the use of organic conductive polymers as the cathode. In one paper, polyaniline (PANI) was used in combination with a chloride-conducting polymer electrolyte. The authors simply spread it on top of the polymer substrate without using any more sophisticated deposition methods. With the polymer matrix polyvinylidene fluoride-hexafluoropolymer (PVDF-HF) as the electrolyte, PANI seemed to function well, although the authors were skeptical about the use of PANI, as no real understanding of the mechanism could be gained. They were also skeptical that the "reduction" would work independently or whether chloride or some other species were involved ^{[60] [61,62] [63]}

A completely different cathode material was proposed by Zhao et al. ^[59], who coated a carbon nanotube substrate with chloride-ion-doped polypyrrole (PPy) using a chemical oxidative polymerization to yield a chloride-ion-doped PPy cathode. A maximum capacity of 118 mAh/g was received. Compared with other CIBS, the capacity did not fade very much, and after 40 cycles, a capacity of 90 mAh/g remained. The system was built in a small pouch cell, which could power a commercially available red LED for more than 5 min. Furthermore, the charge and discharge mechanism were thoroughly examined using electrochemical impedance spectroscopy (EIS) and XPS. The proposed mechanism is shown in Figure 6.

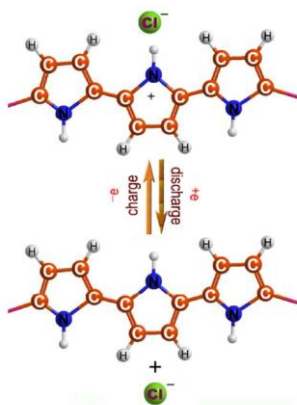


Figure 6: Charge/discharge mechanism proposed by the authors of publication ^[59]

In that paper, the coordination of Cl^- to a N^+ species in the pyrrole was proposed. Further investigation seemed to show that the PPy_{14}^+ cation in the electrolyte and TFSI can also intercalated. This seems to be a normal phenomenon, and the authors cite several studies on this topic. However, this intercalation seemed not to have any dominant effect on the cycling, and the small chloride ion acts as the main charge compensation.

3.5 Progress on the Anode Side

On the anode side, in addition to Li, Mg was investigated ^{[64] [52]}, which was chosen due to abundant sources of Mg ores, its low cost, and, moreover, its ability to provide two electrons per redox reaction. Zhao et al. ^[64] reported using Mg in different forms such as polished Mg foil, but no discharge could be observed. Therefore, two different preparations were used: pure Mg powder, which was ball-milled with carbon black, and MgH_2 ball-milled with carbon black followed by the de-insertion of H_2 .

In addition, Gao et al. ^[52] ball-milled Mg powder with MgCl_2 and carbon black. Their choice to use half-discharged anodes was not explained in the paper, but it can be assumed that it was to decrease the kinetic barrier during chloride migration, which is a method that is also used in fluoride ion batteries ^[10].

In general, all discharge curves for batteries with Mg start with a good OCV of over 2 V followed by a voltage drop; the discharge plateaus generally slope somewhat and are observed between 0.8 V-1.3 V (see Figure 3). Interestingly, both papers propose apparently different mechanisms for VOCl and FeOCl/BiOCl, (see also Table 4).

In the work of Zhao et al., the transformation of Mg to MgCl₂ could be proven by XRD and XPS, while FeOCl and BiOCl should be reduced to the corresponding metal oxides, which is in contrast with the work of Gao et al., wherein the use of a half-charged anode and VOCl followed a different mechanism; namely, VOCl was first charged to VOCl₂ and then redischarged with a two-electron loss to VO.

XRD patterns were recorded at different steps during the discharge, and V₂O₃ is observed, but it was already present in the starting material due to a decomposition reaction during ball-milling. In addition, a drastic decrease in the crystallinity of VOCl was observed during discharge. After ten cycles, the V₂O₃ phase was predominant, and no VO was detected. It was proposed that the VO could be on the nanoscale and thus undetectable by XRD or could have been decomposed to V₂O₃. An XPS analysis was therefore performed. After charging the VOCl electrode, peaks were detected in XPS that could be assigned to V⁴⁺, which indicates VOCl₂. Moreover, two reduction peaks appeared during discharge in the cyclic voltammetry (CV) scan, which confirmed the two-step reduction from VOCl₂ to VOCl to VO.

Both papers on Mg reported problems related to the loss of electrical contact during cycling. This is due to the large volume change of Mg to MgCl₂ (and possibly also due to the formation of insulating MgCl₂).

Zhao et al. also reported that the electrolyte decomposed at the Mg anode and that the decomposition products could form a layer that suppressed chloride transport. The dissolution of Mg ions and the cathode material into the electrolyte were not discussed, and no tests were performed on this decomposition in either paper.

3.6 Room-Temperature (RT) Solid-State CIBs

In the work of Gschwind et al., a completely new approach was proposed to solve the electrode dissolution problem. Instead of developing more stable cathodes, they suggested using polymer electrolytes (Figure 7)
[36].

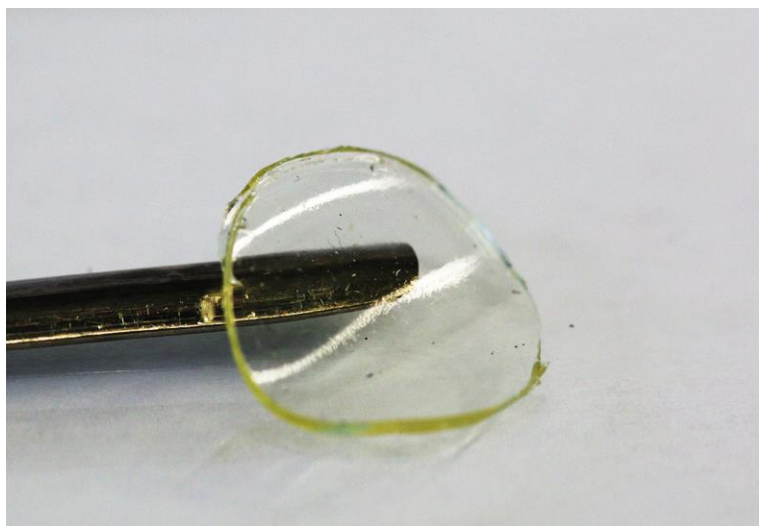


Figure 7: Photograph of one of the polymer electrolytes with a gelatin matrix. Taken from publication^[36]

Three chloride-conducting electrolytes were proposed based on gelatin, PVDF-HF, and polyvinyl chloride (PVC). The conductivity is shown in Figure 8. Different chloride salts were used; tetramethylammonium chloride was used for gelatin, octylammonium chloride for PVDF, and tetrabutylammonium chloride for PVC. The migration of the ions was investigated using EIS. PVC had the worst conductivity of 10⁻⁷ S/cm at

RT, and a dispersive ionic transport was expected at higher frequencies. Its low conductivity was attributed to lower ion mobility as well as a lower total ion concentration. Meanwhile, gelatin and PVDF-HF exhibited conductivities of around 10^{-4} S/cm and similar capacitance values. The Cole–Cole spectra of these two membranes indicated that ionic mobility in these samples occurred on a faster time scale (Figure 8)

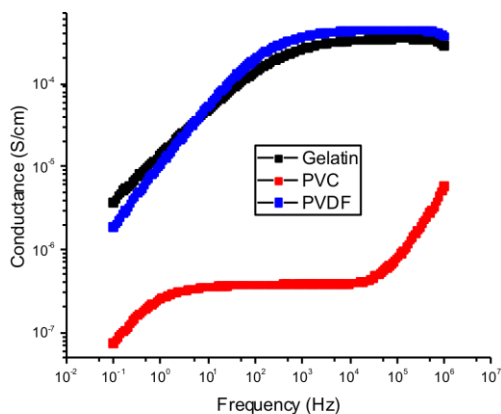


Figure 8: Conductivity Plot of three different chloride-conductive polymer electrolytes. Taken from publication ^[36]

The chloride-conducting membranes were also tested in a very simple battery set up using pieces of Zn as the anode and CuCl_2 or PANI as the cathode material. The respective metal powders were directly pressed onto the surface of the membranes without using more sophisticated preparation techniques. The authors state that even with this primitive method (which provides very bad contact with the active material), a discharge capacity of around 130 mAh/g could be observed. The use of Zn instead of Mg or Li reduced the OCV and the discharge plateau to around 0.8 V. The discharged cells were also investigated. The formation of deposits on the anode was visible by the naked eye, and further SEM analysis demonstrated that “ZnCl” crystallites grew on the first layer of the membranes. The authors were careful to point out that no clear evidence for transformation to elemental copper or Cu(I)Cl could be seen on the cathode side. A test was therefore performed with $\text{BiCl}_3/\text{BiOCl}$, and with this active material, metallic Bi could be detected. In future work, polymer electrolyte could be embedded in the anode and cathode materials and in the polymer matrix to build a fully flexible battery.

3.7 Conclusion of Research State of CIBs

In conclusion, the following can be summarized for CIBs with liquid electrolytes:

- MCl_x salts can provide more than one electron per redox reaction, but they are dissolved by electrolytes based on ILs.
- Li can be used as the anode, but dissolution could also be a problem.
- To avoid dissolution of MCl_x salts, more stable oxychlorides have been proposed.
- Oxychloride salts withstand apparently better the electrolyte and can be cycled for around 25 cycles.
- Furthermore, a Li-free alternative anode based on Mg was also proposed.
- Some preliminary studies were performed on organic cathodes as well as chloride-conducting polymer electrolytes.

However, in corresponding publications many questions remain unresolved, especially the behavior of the electrolyte and the quantity of dissolved electrode material. Moreover, the reduction process on the cathode

side lacks clear evidence. While the presence of metallic Bi could be proven from BiOCl or BiCl₃, Bi₂O₃ or BiO was not clearly shown, nor was the presence FeO or VO. In each case, the missing compounds were attributed to decomposition or the nanoscale size of particles. It would be of significant interest to investigate more deeply these mechanisms. In addition, more research on the electrolyte and the quantity of dissolved electrode materials is necessary. Polymer electrolytes open a very interesting avenue but require significant investigation before they can be used in a fully flexible battery. To be able to further develop these systems, thorough knowledge of the safety and toxicity of the target material is crucial; therefore, in the next section we assess the most common materials used in CIBs.

4. Considerations of Safety, and Toxicity of the Material Used in CIBs

4.1 Introduction and methodologies applied

Novel technologies such as chloride batteries need to be assessed not only in terms of their potential performance, but also in terms of potential hazards they might cause. Detailed information on hazardous materials, such as some battery components, has been made publicly available as a result of the REACH and CLP regulations ^[65] ^[66]. Based on the latter piece on legislation and on the Seveso Directive ^[67], we developed two methodologies for the assessment of potential hazards caused by battery materials ^[68]

The first one of these tools, Hazard Traffic Lights (HTL) is a quick, qualitative method that color-codes the potential hazards of a material based on their signal words: danger, warning, or no hazard word. Suppliers are the ones classifying substances, but in some cases, classification is done at EU level and suppliers must apply this harmonized classification. With slight differences, we had already applied it in ^[8].

The second one, Total Hazard Points (THP) is based on a procedure described in ^[69], which uses the lower tier values (LT)¹ described in the Seveso Directive to rank different materials (or batteries), according to their potential hazardousness. Since the more important a hazard is, the lower its LT is, it is necessary to calculate their inverse to obtain a value which can be used to rank substances easily. We call this figure Hazard Level (HL) and it has units of tons⁻¹. The higher the HL is, the more dangerous the substance.

$$HL = \sum_i^n \frac{1}{LT_i}$$

In a given product or production process, the THP of a given substance would be calculated by multiplying its mass by the HL.

$$THP = \text{mass} * HL$$

Based on publicly available data at the European chemical Agency Database (www.echa.eu), we assessed the potential hazards of most promising materials to be used as cathodes, anodes, and electrolytes in CIBs using HTL and THP (Table 5-7). For the latter, only the HL was calculated, as the actual mass composition of a battery is not known. Of all the materials taken into account, only for the FeOCl there was no hazard information at the ECHA webpage. It is thus, not included in Table 5. All anode materials evaluated were REACH registered, while the majority of electrolytes evaluated were only pre-registered.

¹ For a given hazard, the lower tier is the maximum tonnage of a substance with such potential hazard a facility can store without having to implement a number of safety measurements.

4.2 Results

All three groups of substances may cause several hazards, mostly concerning human health (Tables 5-7). This is to be expected, as hazards to human health make the majority of those described in the CLP regulation^[66]. Still, it is worth highlighting the potential for environmental hazards in cathode materials, and of physical hazards in electrode materials.

Table 5: Hazard Traffic Lights and Hazard Level of cathode materials for Chlorine Ion Batteries

		FeCl ₃	CuCl ₂	VOCl ₃	BiOCl	TiCl ₄	CoCl ₂	NiCl ₂	MnCl ₂	BiCl ₃	
REACH registered?		yes	yes	yes	-	-	-	yes	yes	yes	
HL		0.25	0.24	0.16	0.06	0.45	0.68	0.65	0.16	0.13	
HTL											
Physical hazard	Explosive										
	Flammable										
	Oxidizer										
	Gases under pressure										
	Self-reactive/organic peroxide										
	Pyrophoric										
	Self-heating										
	Water reactant										
	Corrosive to metals										
	Health hazard	Acute toxicity	Oral								
Skin											
Respiratory											
Irritant		Skin									
		Eye									
Sensitization											
Germ cell mutagenicity											
Carcinogenity											
Reproductive toxicity											
Specific target organ toxicity		single exposure									
		repeated exposure									
Aspiration hazard											
Env. Hazard	Hazardous to the aquatic environment	Acute									
		Chronic									




Besides being hazardous to the aquatic life, cathode materials tend to be toxic if ingested, and, some, also if inhaled (Table 5). However the most shared hazard is irritation, to both eye and skin. HTL results suggest Co and Ni chlorides are the two most dangerous electrode materials evaluated. They share the aforementioned hazard with most of the other substances, but they are also carcinogenic, mutagenic and toxic to


reproduction. Opposed to them are the bismuth compounds, BiOCl and BiCl₃, probably the safest cathode materials, since they are the two with the lowest number of reported hazards. This qualitative ranking is supported by the HL results.

Table 6: Hazard Traffic Lights and Hazard Level of anode materials for Chlorine Ion Batteries


		Anodes							
		Mg	Li	Ca	Na	MgCl ₂	LiCl	CaCl	NaCl
REACH registered?		✓	✓	✓	✓	✓	✓	✓	✓
HL		0.21	0.26	0.23	0.23	0.15	0.58	0.06	0.05
HTL									
Physical hazard	Explosive								
	Flammable	Danger	Danger						
	Oxidizer								
	Gases under pressure								
	Self-reactive/organic peroxide								
	Pyrophoric	Danger							
	Self-heating	Danger							
	Water reactant	Danger	Warning	Warning	Warning				
	Corrosive to metals					Warning			
Health hazard	Acute toxicity	Oral		Danger				Warning	Warning
		Skin							
		Respiratory							
	Irritant	Skin	Warning	Warning	Danger	Warning	Warning	Warning	Warning
		Eye	Warning	Warning	Danger	Warning	Danger	Danger	Warning
	Sensitization					Warning			
	Germ cell mutagenicity								
	Carcinogenity								
	Reproductive toxicity						Danger		
	Specific target organ toxicity	single exposure	Warning		Warning	Danger	Warning	Danger	
		repeated exposure						Warning	Warning
Aspiration hazard									
Env. Hazard	Hazardous to the aquatic environment	Acute							
		Chronic	No hazard word	No hazard word				No hazard word	No hazard word



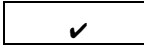
Danger



Warning



No hazard word



Harmonized

Anodes are composed of Group I and II elements, but in an operating battery, their chlorides can also be found there. All alkali and alkali earth metals are skin and eye irritants and, when in contact with water, can release flammable gases (Table 6). With the exception of Li, they are also toxic for specific organs after a single exposure. Their chlorides do not react with water but are still irritants. In addition they tend to be toxic

if ingested. If the pairs M/MCl_n are assessed, Na and Ca could be the safest alternatives according to both HTL and HL results, while Li would be the least desirable one. Exception made for Li, HL for alkali and alkali earths are lower than their chlorides. While the user is not expected either form, a hazard reduction would be expected while the battery is in operation, as alkalis and alkali earths are chlorinated.

Table 7: Hazard Traffic Lights and Hazard Level of electrolytes for Chlorine Ion Batteries

		Electrolytes						
		NH ₄ Cl	TBA Cl	Epoxi resin	PVC	PVDF	PANI	Ppy*
REACH registered?		✓						
HL		0.19	0.07	0.05	0.28	0.05	0.13	0.15
HTL								
Physical hazard	Explosive							
	Flammable							
	Oxidizer							
	Gases under pressure							
	Self-reactive/organic peroxide							
	Pyrophoric							
	Self-heating							
	Water reactant							
	Corrosive to metals							
Health hazard	Acute toxicity	Oral	✓					
		Skin						
		Respiratory						
	Irritant	Skin						
		Eye	✓					
	Sensitization							
	Germ cell mutagenicity							
	Carcinogenity							
	Reproductive toxicity							
	Specific target organ toxicity	single exposure						
		repeated exposure						
Aspiration hazard								
Env. Hazard	Hazardous to the aquatic environment	Acute						
		Chronic						



* The monomer pyrrole is used as proxy

TBACl: Tetrabutylammonium chloride, PVC: Polyvinylchloride, PVDF: Polyvinyl difluoride , PANI: Polyaniline, Ppy: Polypyrrole

The electrolytes evaluated can be grouped into chlorides: NH_4Cl , tetrabutylammonium chloride (TBACl) and gels: epoxy resin, PVC, PVDF, PANI, and PPy (Table 7). The former are both toxic if ingested or inhaled as well as toxic to specific organs after a single exposure. They are also eye and skin irritants, and so are four of the gels evaluated. Due to the additional potential hazards, NH_4Cl is probably the most dangerous of the chlorides assessed, while PPy is it for the gels. PPy is the only gel that is not skin irritant, but is a strong eye irritant and an acute toxic regardless of the mean of exposure.

4.3 Discussion and recommendations

HL results indicate cathode materials would be the most hazardous element of a chloride ion battery, followed by anode materials and electrolytes (average HLs are 0.31, 0.24, and 0.13 respectively). As mentioned in previous works^[8], this does not mean the use of chloride batteries is dangerous. However, it is worth remembering batteries, as almost any piece of modern technology, contain materials that can be dangerous at some point during the product's life cycle. The user might never be exposed to these substances, but the producer or the dismantler might.

Lack of mass composition prevented us from conducting a THP of different battery configurations. For a given performance (energy stored, power, lifetime, etc.), small amounts of a very hazardous material might be safer than larger amount of less dangerous materials. That said, if a 1:1:1 cathode, anode, and electrode combination is assumed, $\text{BiOCl}/\text{Na}/\text{Epoxid}$ or PVDF would be the safest alternative (THP of 0.34) while the most hazardous one would be $\text{CoCl}_2/\text{Li}/\text{PVC}$ (THP of 1.22). The substantial difference between both configurations stressed the need to take into account safety aspects when selecting battery materials.

5. Future Development and Outlook

In general, CIBs currently achieve an approximate average discharge of 80 mAh/g, an average nominal discharge slightly below 2 V, and about two dozen cycles. Therefore, it may be suggested that in terms of discharge voltage and capacity, this performance lies somewhere between those of standard alkaline batteries and lead-acid batteries. However, the CIBs developed thus far use expensive electrolytes (instead of inexpensive KOH or H_2SO_4) and require inert techniques. Moreover, the use of high-temperature synthesis for VOCl, carbon nanotubes, and metallic Li make CIBs far more expensive.

Theoretically, CIBs can achieve a good capacity, but their practical realization will require a great deal of research. However, the most significant advantage of CIBs is the abundance of chloride-containing materials and their availability worldwide, which not only lowers costs but also enables manufacturing all over the world. Furthermore, due to the stability of chloride ions, air-stable systems should be possible. We believe that the most important areas of focus should be (a) the stability of the material in air, (b) long, reliable cycling capability, (c) easily available material, and (d) safety.

A battery combining all these attributes (even if discharge voltage does not exceed 2.5 V) could possibly lead to affordable, and large-storage batteries. Nevertheless, predicting the development of cell construction in CIBs is very difficult, but we can propose a series of materials that could be worth investigating:

For the electrolyte, there are numerous possibilities involving changing the cation and tuning the solubility and reactivity of the salt, especially for organic chloride salts. We think that research in this direction could potentially provide chloride organic salts that are more suitable than the commercially available ones.

A similar strategy would be to develop RT ionic liquids, i.e., organic chloride salts that are liquid at RT. A few chloride-containing ILs such as octylimidazolium methyl chloride are commercially available, which was used in CIBs. However, most of them are very viscous and must be dissolved in another ionic liquid. Nevertheless, many options are available, and a CIB with a RT ionic liquid would exhibit well-known advantages, such as their low flammability, etc. Furthermore, the choice to use polymer electrolytes is of considerable interest, and the literature on Li ion polymer electrolyte indicates that many polymer matrixes are available that could be used to transport chloride ions ^[70] ^[71] ^[37] ^[72]. These polymers can be further tailored to the specific needs of the application. In addition, polymers with a fixed cation on the polymer backbone would make ideal candidates, such as polypyridinium salts. According to Watanabe et al. ^[32], these polymers also be mixed with other chloride salts to increase the conductivity. Moreover, the use of polymer blends to form anionic ionomer membranes ^[73] with PVA and ammonium chloride salt was proposed in the literature and could possibly be adapted for chloride conduction.

Simple inorganic salts as CuCl_2 or FeCl_3 are the most attractive material for the cathode, because they are inexpensive, easy to obtain, and exhibit good values in theoretical calculations. We think that these types of salt remain the most attractive. Further efforts might be devoted to finding better cathode mixtures and preparation methods to ensure high electrical and ionic conductivity. Stabilization of the structure during dechlorination would be also very beneficial since large volume changes and volume effects will generally damage the grains and particles, leading to a loss of contact. This could also be partially solved with different particle morphology. A new avenue of development, which seems to be open is the use of organic cathode materials such as PANI and PPy, as mentioned above. These are very attractive and have already demonstrated promising results, but these materials are well known to exhibit long-term stability problems in all-organic batteries due to their ability to change oxidation state.

An intercalation material similar to those used for LIBs would be another attractive candidate. Unfortunately, to the best of our knowledge, no suitable chloride intercalation compound similar to graphite electrode in LIB has been found. In our work, we have attempted several coordination materials for this purpose such as copper complexes or aluminum complexes, but we have not had success until now.

Ideally, a metal possessing the ability to exhibit several oxidation states would be used, such as manganese. The coordination compound should be designed so that the chloride ions are located in the second coordination sphere and cannot directly form ionic bonds. A compound that could exhibit chlorination and dechlorination processes and a sufficiently positive redox potential could form an attractive cathode material.

For anode systems, several materials can be suggested, such as foamed metals, to provide a large surface area for the formation of metal chlorides, although a reversible reaction must be possible. Using intercalation-type compounds are another potential strategy, but to the best of our knowledge, no such materials exist at present. Another possibility could be to use coordination compounds or organic electrodes for the anode materials, as proposed above for the cathode materials.

Overall, we showed that in addition to being theoretically interesting, the research on halogenide conductors demonstrates that CIB systems could truly be an alternative to current commercial batteries.

Acknowledgement

The authors want to thank Maximilian Fichtner, Marcel Weil, and Axel Gross for their support.

References:

- [1] D. Linden, T. B. Reddy, *Handbook of Batteries*, New York, **2001**.
- [2] D. Berndt, D. Spahbier, *Batteries I. General*, **2014**.
- [3] M. Tarascon, M. Armand, *Nature* **2001**, *414*, 359–367.
- [4] A. Ponrouch, C. Frontera, F. Bardé, M. R. Palacin, *Nature Materials* **2016**, 162–172.
- [5] R. C. Massé, E. Uchaker, G. Cao, *Science China Materials* **2016**, *58*, 715–766.
- [6] N. Yabuuchi, K. Kubota, M. Dahbi, S. Komaba, *Chem. Rev.* **2014**, *114*, 11636–11682.
- [7] M. M. Hiue, D. C. Bock, E. S. Takeuchi, A. C. Marschilok, K. J. Takeuchi, *Coordination Chemistry Reviews* **2015**, *287*, 15–27.
- [8] F. Gschwind, G. Rodriguez-Garcia, D. J. S. Sandbeck, A. Gross, M. Weil, M. Fichtner, N. Hörmann, *Journal of Fluorine Chemistry* **2016**, *182*, 76–90.
- [9] M. A. Reddy, M. Fichtner, *J. Mater. Chem.* **2011**, *21*, 17059–17062.
- [10] C. Rongeat, M. A. Reddy, T. Diemant, R. J. Behm, M. Fichtner, *Journal of Materials Chemistry A* **2014**, *2*, 20861–20872.
- [11] L. Zhang, M. Anji Reddy, M. Fichtner, *Solid State Ionics* **2015**, *272*, 39–44.
- [12] J. Chable, A. G. Martin, A. Bourdin, M. Body, C. Legein, A. Jouanneaux, M. P. Crosnier-Lopez, C. Galven, B. Dieudonné, M. Leblanc, et al., *Journal of Alloys and Compounds* **2016**, DOI 10.1016/j.jallcom.2016.09.135.
- [13] F. Gschwind, J. Bastien, *Journal of Materials Chemistry A* **2015**, *3*, 5628–5634.
- [14] D. Steinle, L. Friedrich, N. Bevilacqua, E. von Hauff, F. Gschwind, *Materials 2016, Vol. 9, Page 965* **2016**, *9*, 965.
- [15] F. Gschwind, Z. Zao-Karger, M. Fichtner, *J. Mater. Chem. A* **2014**, *2*, 1214–1218.
- [16] A. Grenier, A. G. Porras Gutierrez, H. Groult, D. Dambournet, *Journal of Fluorine Chemistry* **2016**, *191*, 23–28.
- [17] M.-C. Lin, M. Gong, B. Lu, Y. Wu, D.-Y. Wang, M. Guan, M. Angell, C. Chen, J. Yang, B.-J. Hwang, et al., *Nature* **2015**, *520*, 324–328.
- [18] W. Wang, B. Jiang, W. Xiong, H. Sun, Z. Lin, L. Hu, J. Tu, J. Hou, H. Zhu, S. Jiao, *Scientific Reports* **2013**, *3*.
- [19] a) A. Jain, S. P. Ong, G. Hautier, W. Chen, W. D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder, et al., *APL Materials* **2013**, *1*, 011002.

- b) S. P. Ong, W. D. Richards, G. Hautier, M. Kocher, S. Cholia, D. Gunter, V. L. Chevrier, K. A. Persson, G. Ceder, *Comput. Mater. Sci.* **2013**, *38*, 314–319.
- [20] H. Hoshino, M. Yamazaki, Y. Nakamura, M. Shimoji, *J. Phys. Soc. Jpn.* **1969**, *26*, 1422–1426. and reference herein
- [21] J. Mizusaki, K. Arai, K. Fueki, *Solid State Ionics* **1983**, *11*, 203–211.
- [22] S. Palchoudhuri, G. K. Bichile, *Journal of materials science letters* **1987**.
- [23] C. E. Derrington, A. Lindner, M. O'Keeffe, *Journal of Solid State Chemistry* **1975**, *15*, 171–174.
- [24] K. Okamoto, *Solid State Ionics* **2002**, *154-155*, 577–580.
- [25] N. Imanaka, K. Okamoto, G. Y. Adachi, *Angew. Chem. Int. Ed.* **2002**, *41*, 3890–3892.
- [26] I. V. Murin, O. V. Glumov, N. A. Mel'nikova, *Russ J Electrochem* **2009**, *45*, 411–416.
- [27] C. Rongeat, M. A. Reddy, R. Witter, M. Fichtner, *J. Phys. Chem. C* **2013**, *117*, 4943–4950.
- [28] C. Rongeat, M. A. Reddy, R. Witter, M. Fichtner, *ACS Appl. Mater. Interfaces* **2014**, *6*, 2103–2110.
- [29] D. NEWMAN, D. HAZLETT, K. MUCKER, *Solid State Ionics* **1981**, *3-4*, 389–392.
- [30] M. Fujimoto, T. Nogami, H. Mikawa, *Chemistry Letters* **1982**, *11*, 547–550.
- [31] M. Fujimoto, T. Nogami, H. Mikawa, *Solid State Ionics* **1984**, *11*, 313–315.
- [32] M. Watanabe, S.-I. Yamada, K. Sanui, N. Ogata, *J. Chem. Soc., Chem. Commun.* **1993**, *0*, 929–931.
- [33] L. C. Hardy, D. F. Shriver, *Macromolecules* **1984**, *17*, 975–977.
- [34] J. Qiao, J. Zhang, J. Zhang, J. Zhang, *Journal of Power Sources* **2013**, *237*, 1–4.
- [35] *Inorganic Syntheses*, John Wiley & Sons, Inc., Hoboken, NJ, USA, **1989**.
- [36] F. Gschwind, D. Steinle, D. Sandbeck, C. Schmidt, E. von Hauff, *ChemistryOpen* **2016**, *5*, 525–530.
- [37] Jae Ho Shin, Hyo Lin Lee, Sung Ho Cho, Jeonghan Ha, A. Hakhyun Nam, G. S. Cha, *Anal. Chem.* **2004**, *76*, 4217–4222.
- [38] N. P. Illsley, A. S. Verkman, *biochemistry* **2001**, *26*, 1215–1219.
- [39] F. Zapata, A. Caballero, A. Espinosa, A. Tárraga, P. Molina, *J. Org. Chem.* **2008**, *73*, 4034–4044.
- [40] N. Imanaka, K. Okamoto, G. Y. Adachi, *Electrochemistry Communications* **2001**, *3*, 49–51.
- [41] K. P. Xiao, P. Bühlmann, S. Nishizawa, S. Amemiya, Y. Umezawa, *Anal. Chem.* **1997**, *69*, 1038–1044.
- [42] R. A. Frizzell, M. J. Koch, S. G. Schultz, *J. Membrin Biol.* **1976**, *27*, 297–316.
- [43] R. A. Frizzell, M. Field, S. G. Schultz, *Am. J. Physiol.* **1979**, *236*, F1–8.
- [44] P. Silva, J. Stoff, M. Field, L. Fine, *American Journal of ...* **1977**.
- [45] G. Merle, M. Wessling, K. Nijmeijer, *Journal of Membrane Science* **2011**, *377*, 1–35.
- [46] V. K. Shahi, S. K. Thampy, R. Rangarajan, *Journal of Membrane Science* **1999**, *158*, 77–83.
- [47] P. F. McGrath, R. D. Hooton, *Cement and Concrete Research* **1996**, *26*, 1239–1244.
- [48] C. C. Yang, *Cement and Concrete Research* **2006**, *36*, 1304–1311.
- [49] K. Audenaert, Q. Yuan, G. De Schutter, *Construction and Building Materials* **2010**, *24*, 396–402.
- [50] X. Zhao, S. Ren, M. Bruns, M. Fichtner, *Journal of Power Sources* **2014**, *245*, 706–711.
- [51] X. Zhao, Z. Zhao-Karger, D. Wang, M. Fichtner, *Angew. Chem. Int. Ed.* **2013**, *52*, 13621–13624.
- [52] P. Gao, X. Zhao, Z. Zhao-Karger, T. Diemant, R. J. Behm, M. Fichtner, *ACS Appl. Mater. Interfaces* **2014**, *6*, 22430–22435.
- [53] P. Gao, M. A. Reddy, X. Mu, T. Diemant, L. Zhang, Z. Zhao-Karger, V. S. K. Chakravadhanula, O. Clemens, R. J. Behm, M. Fichtner, *Angew. Chem.* **2016**, *128*, 4357–4362.
- [54] P. Gao, X.-M. Lin, M. A. Reddy, Le Zhang, T. Diemant, R. J. Behm, M. Fichtner, *J. Electrochem. Soc.* **2016**, *163*, A2326–A2332.

- [55] V. Varadaraajan, B. C. Satishkumar, J. Nanda, P. Mohanty, *Journal of Power Sources* **2011**, *196*, 10704–10711.
- [56] S. H. Ng, S. Y. Chew, J. Wang, D. Wexler, Y. Tournayre, K. Konstantinov, H. K. Liu, *Journal of Power Sources* **2007**, *174*, 1032–1035.
- [57] P. Gao, C. Wall, L. Zhang, M. A. Reddy, M. Fichtner, *Electrochemistry Communications* **2015**, *60*, 180–184.
- [58] C. B. Minella, P. Gao, Z. Zhao-Karger, X. Mu, T. Diemant, M. Pfeiffer, V. S. K. Chakravadhanula, R. J. Behm, M. Fichtner, *ChemElektroChem* **2017**, DOI 10.1002/celec.201700034.
- [59] X. Zhao, Z. Zhao, M. Yang, H. Xia, T. Yu, X. Shen, *ACS Appl. Mater. Interfaces* **2017**, acsami.6b14755.
- [60] H. Karami, M. F. Mousavi, M. Shamsipur, *Journal of Power Sources* **2003**, *117*, 255–259.
- [61] S. Li, G. Zhang, G. Jing, J. Kan, *Synthetic Metals* **2008**, *158*, 242–245.
- [62] Y. Xia, D. Zhu, S. Si, D. Li, S. Wu, *Journal of Power Sources* **2015**, *283*, 125–131.
- [63] B. H. Shambharkar, S. S. Umare, *Materials Science and Engineering: B* **2010**, *175*, 120–128.
- [64] X. Zhao, Q. Li, Z. Zhao-Karger, P. Gao, K. Fink, X. Shen, M. Fichtner, *ACS Appl. Mater. Interfaces* **2014**, *6*, 10997–11000.
- [65] EU, Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93, 2006
- [66] EC, Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006, 2008.
- [67] EU, Directive 2012/18/EU of the European Parliament and of the Council of 4 July 2012 on the control of major-accident hazards involving dangerous substances, amending and subsequently repealing Council Directive 96/82/EC, 2012.
- [68] G. Rodriguez-Garcia, J. Braun, J.F. Peters, M. Weil, Hazard statements: looking for alternatives to toxicity evaluation using LCA, *Metall. Res. Technol.* (submitted).
- [69] H. Stahl, D. Bauknecht, A. Hermann, W. Jenseit, A.R. Köhler, C. Merz, et al., *Ableitung von Recycling- und Umweltaanforderungen und Strategien zur Vermeidung von Versorgungsrisiken bei innovativen Energiespeichern (Determination of recycling and environmental requirements and strategies to avoid supply risks with innovative energy storage)*, Umweltbundesamt, Des-sau-Roßlau (Germany), 2016
- [70] J. Y. Song, Y. Y. Wang, C. C. Wang, *Journal of Power Sources* **1999**, *77*, 189–197.
- [71] Y.-L. S. Tse, H. N. Sarode, G. E. Lindberg, T. A. Witten, Y. Yang, A. M. Herring, G. A. Voth, *J. Phys. Chem. C* **2014**, *118*, 845–853.
- [72] D. F. Vieira, C. O. Avellaneda, A. Pawlicka, *Electrochimica Acta* **2007**, *53*, 1404–1408.
- [73] C.-C. Yang, G.-M. Wu, S.-J. Lin, *J Appl Electrochem* **2006**, *36*, 655–661.