

Final Draft of the original manuscript

Wang, L.; Snihirova, D.; Deng, M.; Wang, C.; Höche, D.; Lamaka, S.; Zheludkevich, M.:

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In: Electrochimica Acta. Vol. 373 (2021) 137916.

First published online by Elsevier: 05.02.2021

https://dx.doi.org/10.1016/j.electacta.2021.137916

1	Indium chloride as an electrolyte additive for primary aqueous Mg
2	batteries
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10	Abstract: Indium chloride (InCl ₃) as an electrolyte additive for primary aqueous Mg batteries
11	is evaluated in this work in terms of its effect on discharge potential, self-corrosion rate and
12	utilization efficiency of a newly developed Mg-0.15Ca anode. InCl ₃ addition to aqueous
13	electrolyte leads to a more negative discharge potential but the enhancement weakens along
14	with the consumption of In^{3+} to form $In(OH)_3$ precipitates during the discharge process.
15	Utilization efficiency of the anode is increased by adding InCl ₃ due to uniform anodic
16	dissolution and suppressed self-corrosion with reduced chunk effect. Mg-air battery test results
17	indicate that 10 mM InCl ₃ as electrolyte additive significantly enhances the cell voltage of
18	aqueous Mg-air battery to 1.74 V and the specific energy based on anode weight loss to 2.26
19	kWh/ kg at 1 mA cm ⁻² .
20	
21	
22	
23	Key words: primary aqueous Mg batteries; electrolyte additive; local pH measurement; self-
24	corrosion.

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1 1. Introduction

2 Metallic Mg possesses attractive electrochemical characteristics as an electrode material for energy storage, like the acknowledged highly negative redox potential ($-2.37 V_{SHE}$) and high 3 4 volumetric capacity (3832 mA h cm⁻³) [1-3]. Owing to the huge potential as power sources 5 for marine equipment and as standby emergency energy suppliers for schools, hospitals, etc., 6 aqueous Mg batteries have been the subjects of intense research in recent years [4-14]. 7 Meanwhile, some new applications of aqueous Mg batteries have been proposed and evaluated 8 lately, such as acting as the power supply for transient implantable devices [15], electronic 9 contact lenses [16] and urine purifying [17]. The practical performance of aqueous Mg batteries 10 still leaves much to be desired due to two major issues, i.e. large overvoltage caused by sluggish 11 anodic and cathodic reaction kinetics and fast self-corrosion of Mg anodes in aqueous 12 electrolytes. In this context, many approaches from diverse aspects aiming of performance 13 boost regarding Mg-based batteries have been proposed, including anodes design [4-6, 18-20], electrolyte modification [21-27] and cathode catalysts optimization [28-30]. Among these 14 approaches, electrolyte modification has attracted much attention in recent years. Some 15 improvements have been achieved by electrolytes modification in terms of introducing diverse 16 17 chemical reagents into the electrolytes. Generally, the conventional electrolyte additives for 18 aqueous Mg batteries are required with capability of inhibiting the corrosion of Mg to enhance 19 the anodic utilization efficiency and, thus, the capacity and energy density of the battery. As 20 reported by Deyab [24], the adoption of 2.5 mM decyl glucoside, which is a kind of corrosion 21 inhibitor of Mg, improved the utilization efficiency of pure Mg in concentrated NaCl electrolyte, from 36.9% to 86.2% at 5 mA cm⁻². Ma and co-workers found the addition of 22 sodium phosphate and sodium dodecylbenzenesulfonate enhances the anodic efficiency of 23 AZ91 anode in 3.5 wt.% NaCl solution from 44.1% to 48.7% with ~1.1 V discharge voltage at 24 20 mA cm⁻² current density [31]. Both decyl glucoside and sodium dodecylbenzenesulfonate 25

1 are surfactant, which are capable of adsorbing on Mg anode to act as inhibitors. Thus, the 2 utilization efficiency of Mg anode can be improved. Lately, Höche and co-workers [22] 3 proposed a novel idea for selecting electrolyte additives for aqueous Mg batteries, which mainly focuses on Fe^{2+}/Fe^{3+} complexing agents that are able to prevent the re-deposition of Fe, 4 which is typical corrosion inducing impurity in Mg. The self-corrosion rate of Mg anode was 5 6 reduced due to the retardation of Fe re-deposition [32-34]. Meanwhile, battery voltage is improved since the selected chemical agents are capable of forming complexes with Mg^{2+} and, 7 thus, the film-relevant overvoltage is reduced. Vaghefinazari et al. [26] and Wang et al. [27] 8 9 both reported great enhancement of battery voltage for aqueous Mg-air system with commercially pure Mg and Mg-Ca anodes by Mg²⁺ complexing agents, e.g. Tiron, NTA, 5-10 11 sulfosalicylate and 3,4-dihydroxybenzoate. For instance, the voltage of Mg-air battery was 1.86 12 V in 5-sulfosalicylate-containing electrolyte in comparison to 1.59 V in blank NaCl solution at 0.5 mA cm⁻² current density [27]. Nevertheless, some of them may also introduce the loss of 13 14 anodic utilization efficiency under specific current density. The addition of 3,4dihydroxybenzoate into 3.5 wt.% NaCl electrolyte at 1 mA cm⁻² current density tremendously 15 decreases the utilization efficiency of Mg-0.04 wt.% Ca anode from 53% to 9%, but it increases 16 the utilization efficiency of the same anode from 59.7% to 62.3% under 10 mA $\rm cm^{-2}$ current 17 density. Thus, these issues could be solved by parameter optimization (additive concentration 18 19 and initial pH) and battery design. Nevertheless, searching for new high-quality additives based 20 on different working mechanism still requires more efforts [35].

Indium (In) alloying is a successful way for activating Al-based aqueous batteries because In³⁺ can re-deposit onto Al anode surface [36-39]. The influence of In as an alloying element on the discharge performance of Mg anodes (particularly Mg-Al-based) has thereby been investigated in recent years [19, 40-43], demonstrating a degree of enhancements on discharge voltage but rare improvements regarding the anode utilization efficiency. Newly developed Mg-Ca-In anode exhibits not only superior discharge voltage but also excellent anodic
efficiency, 80.2% [44]. The activation of Mg anodes induced by In alloying was proposed to
be resulted from In³⁺ re-deposition on the anode surface by the following replacement reaction
[41].

$$3Mg + 2In^{3+} = 3Mg^{2+} + 2In \tag{1}$$

The In³⁺ ions produced by Mg-In alloy dissolution re-deposited back to the anode surface, 6 7 leading to a less-protective surface film and faster dissolution of anode substrate due to 8 formation of micro-galvanic corrosion couples. This research sparked the idea in our group that the existence of In^{3+} ions in the electrolyte could be the key point for the improvement of anode 9 discharge performance. Recently, Gore et al. [45] investigated the anodic activation of a high 10 purity Mg in diluted NaCl solution (0.1 M) with the presence of In³⁺. As reported, 1 mM InCl₃ 11 12 addition accelerated anodic dissolution but did not change the cathodic kinetics of Mg under 13 polarization. Hence, the authors recommended that InCl₃ is a potential additive to develop aqueous Mg batteries with high performance. In that work, more emphasis was put on the effect 14 15 of InCl₃ on the anodic and cathodic kinetics of Mg by performing potentiodynamic polarization 16 tests and few discharge tests have been done to evaluate the improvement of Mg battery introduced by InCl₃ addition. Moreover, the working mechanism of InCl₃ as cathodic reaction 17 18 inhibitor via the formation of In(OH)₃ has been proposed.

In this work, we thoroughly evaluate the possibility of using InCl₃ as an electrolyte additive for aqueous Mg batteries. The anode material adopted herein is a newly developed binary Mg-0.15Ca alloy with high performance previously proposed by our group [4, 8, 46]. The effect of InCl₃ on discharge potential, self-corrosion rate and utilization efficiency of Mg-0.15Ca anode in 3.5 wt.% NaCl solution is investigated. The working mechanism of InCl₃ as electrolyte additives is thoroughly discussed. Accordingly, the concentration of InCl₃ is optimized and then the Mg-air battery performance is evaluated in the electrolyte with optimum concentration
 of InCl₃.

3 2. Experimental section

4 **2.1 Materials and electrolyte**

A binary Mg-0.15Ca (wt.%) alloy was produced by direct chill casting and used as the anode material. Pure Mg (99.96 wt.%) and pure Ca (99.9 wt.%) were melted under protection of Ar/SF₆ gas in a steel crucible at 760 °C. The melts were then poured into a 700 °C preheated steel mold coated with boron nitride. Immediately, the mold was then immersed into a flowing water bath with a descending speed of 15 cm min⁻¹ for solidification. The actual composition of the prepared alloy is shown in Table 1. The contents of Fe, Ni and Cu impurities were controlled below the traditional accepted tolerance limits [47].

12 (Table 1)

133.5 wt.% NaCl solution with unbuffered pH 5.6 ± 0.1 was used as the background electrolyte.14InCl₃ as electrolyte additive was introduced into the background solution with concentration of151, 5 and 10 mM. The InCl₃-containing electrolytes were unbuffered showing pH of 4.4 ± 0.1 ,16 4.1 ± 0.1 and 3.9 ± 0.1 corresponding to 1, 5 and 10 mM, respectively. All the electrolytes were17prepared by chemical reagents purchased from Sigma-Aldrich and deionized water.

18 2.2 Half-cell discharge test

Discharge testing in half-cell was carried out in a three-electrode cell composed of a KClsaturated Ag/AgCl reference electrode, a Pt counter electrode and the Mg-0.15Ca working electrode with 15×15 mm exposed surface area. Discharge potential of the Mg-0.15Ca anode in the electrolyte with and without InCl₃ at a constant current density (1 mA cm⁻²) was recorded by Gamry Interface 1000 potentiostat. After half-cell discharge testing, utilization efficiency and discharge capacity were calculated based on the mass loss of the anode amid the complete
 discharge period via the following equations,

Utilization efficiency = $\frac{m_{dis}}{\Delta m} \times 100\%$ (2)

3

$$m_{dis} = \frac{I \times t \times M}{F \times n} \tag{3}$$

Specific capacity
$$= \frac{I \times t}{\Delta m}$$
 (4)

6 Where m_{dis} and Δm represent the Faradaic mass loss of anode due to applied discharge current 7 *I* and the actual mass loss respectively, *t* is the discharge time and *F* represents the Faraday 8 constant (26.8 Ah mol⁻¹). *M* and *n* are the atomic mass and the ionic valence for Mg. In order 9 to obtain accurate mass loss, anode samples after discharge were immersed into chromic acid 10 aqueous solution (200 g l⁻¹) for 10 min to remove discharge products and then rinsed with 11 ethanol. Afterwards, the anode mass loss was determined via comparing the sample mass prior 12 to discharge and after removal of discharge products.

13 **2.3 Electrochemical impedance spectroscopy (EIS)**

EIS measurements at open circuit potential (OCP) after discharge for a specific period (1, 5 and 24 h) were also performed by Gamry Interface 1000 potentiostat to evaluate the surface condition alteration of the anode. The applied frequency ranged from 10⁵-10⁻¹ Hz, while a perturbation voltage of 10 mV rms was used.

18 **2.4 Hydrogen evolution test under polarization**

19 Effect of $InCl_3$ on the self-corrosion of Mg-0.15Ca anode during discharge was investigated 20 by the real-time hydrogen evolution test under galvanostatic polarization. Evolved hydrogen 21 gas from Mg-0.15 Ca sample under 1 mA cm⁻² constant current density was collected with a 22 common eudiometer-like set-up previously used in published work [9]. Briefly, the working electrode was also the Mg-0.15Ca sample with 15×15 mm exposed surface area. Volume of the produced H₂ was easily recorded from an inverted burette with minimum scale of 0.1 ml.

3 2.5 Surface analysis

4 The anode surface and cross-sectional morphologies after discharge were characterized by a 5 scanning electron microscope (SEM, TESCAN VEGA 3). Elemental mapping was carried out 6 for selected regions via SEM under backscattered-electron (BSE) mode at 15 kV. Additionally, 7 the morphology anode surface after removal of discharge products was observed under 8 secondary electron (SE) mode in SEM. 3D reconstruction for the surface topography without 9 discharge products was conducted via SEM combined with Mex program (Bruker Alicona) for 10 images processing. Depth profiles were obtained to examine the surface roughness and homogeneity. 11

12 **2.6 Local pH measurement**

13 The local pH of Mg-0.15Ca anode in 3.5 wt. % NaCl with and without InCl₃ under 1 mA cm⁻² galvanostatic polarization was measured via a glass-type pH microelectrode with a tip 14 diameter of 10 µm (pH-10, Unisense), which was calibrated daily. The pH microelectrode was 15 16 fixed at 20 µm above the Mg-0.15Ca sample with approximately 1 mm diameter in order to 17 record the real-time evolution of local pH during galvanostatic polarization. The applied current density was 1 mA cm⁻² with the same configuration adopted in half-cell discharge test. 18 19 The local information for Mg-0.15Ca sample surface was acquired on a sample-centered area 20 $(2000 \,\mu\text{m} \times 2000 \,\mu\text{m})$ at 50 μm above it to demonstrate the distribution of local pH on polarized Mg-0.15Ca surface. All the relevant data was acquired by LV4 software (Science Wares). A 21 22 commercial SVET-SIET system (Applicable Electronics) is employed for the positioning and movement of the pH microelectrode. 23

1 **2.7 Mg-air battery test**

2 At last, the viability of InCl₃ as an electrolyte additive for aqueous Mg batteries was 3 evaluated in a lab-made Mg-air cell. A commercially available air cathode with MnO₂/C catalyst (Gaskatel GmbH) was used as cathode. The working surface was square of 15×15 4 5 mm for the Mg-0.15Ca anode, while round with 18 mm diameter for the cathode. The anode-6 to-cathode distance was kept the same for all discharge tests. Discharge curves of the battery 7 in electrolytes with and without InCl₃ additive were recorded by IVIUM OctoStat at constant 8 current densities. Specific energy of Mg-air batteries were calculated according to the anode 9 mass loss and the equation is expressed as,

10 Specific energy =
$$\frac{\int_0^t I \times U \times \Delta t}{\Delta m}$$
 (5)

11 Where *I*, *t* and Δm are the same meaning as above mentioned. *U* represents the cell voltage.

12 **3. Results and discussion**

13 **3.1 Half-cell discharge performance**

14 In order to evaluate the influence of various concentrations of $InCl_3$ on the discharge 15 performance of the Mg-0.15Ca alloy, half-cell discharge tests were performed. Fig. 1a shows 16 the discharge curves of the Mg-0.15Ca anode in NaCl electrolyte with and without InCl₃. In blank NaCl electrolyte, the discharge potential is relatively stable (- 1.61 V_{Ag/AgCl}) during the 17 18 whole discharge period following a positive shift at the initial 0.5 h stage. By contrast, in the 19 electrolyte with 1 mM and 5 mM InCl₃, a short-term move of the potential towards more 20 negative value appears at the beginning, after which the potential starts to shift positively. 21 Subsequently, the potential remains relatively stable after around 2 h and 14 h in the solution 22 with 1 mM and 5 mM InCl₃, respectively, and the steady potential $(-1.63 V_{Ag/AgCl})$ has no large 23 difference with that in blank NaCl solution. Differently, the addition of 10 mM InCl₃ enables the anode to maintain a significantly more negative potential (-1.76 V_{Ag/AgCl}) during the whole 24

1 24 h discharging process. The results indicate that addition of $InCl_3$ is able to improve the 2 discharge potential of the Mg-0.15Ca anode, but the enhancement effect may weaken along 3 with the continuous discharging. Higher concentration of InCl₃ not only imparts greater 4 improvement on discharge potential but also slows down the weakening of the enhancement 5 effect induced by InCl₃ additive. It is noteworthy that the bulk pH of blank NaCl solution increases from 5.6 \pm 0.1 to 10.4 \pm 0.1 amid 24 h discharge test whereas the final bulk pH of 6 7 InCl₃-containing electrolytes remains below 5. This suggests that InCl₃ has strong pH buffering 8 effect for the electrolyte alkalization amid discharge. Nevertheless, Mg-0.15Ca anode in InCl₃-9 containing electrolytes with similar final pH presented distinct discharge behavior, which will 10 be discussed in the following section. Fig. 1b illustrates the utilization efficiency of the Mg-0.15Ca anode as well as the capacity after discharge at 1 mA cm⁻² for 24 h in NaCl electrolyte 11 12 with and without InCl₃. Addition of 1 and 5 mM InCl₃ increases the utilization efficiency and 13 capacity of the Mg-0.15Ca anode, while addition of 10 mM InCl₃ does not impart any negative 14 effect on the utilization efficiency. Nevertheless, Mg-0.15Ca in NaCl with 10 mM InCl₃ 15 presents the most negative potential. Thus, the best comprehensive discharge performance of Mg-0.15Ca anode is achieved by addition of 10 mM InCl₃. 16

17

(Fig. 1)

18 **3.2 Evolution of anode surface state in InCl3-containing electrolytes**

The change of discharge potential often correlates to the alteration of surface state of the anode. Thus, EIS measurements were performed on the anode after different discharge periods to check the alteration of the anode surface condition by the discharge, as presented in Fig. 2. Obviously, with increasing discharge time the low frequency impedance of the anode in blank NaCl solution decreases (Fig. 2a). Seemingly, the lower impedance may imply that the thin surface film at the interface becomes less protective with increasing discharge time. Additionally, the increase of actual surface area due to anode dissolution also contributes to

1 the lowering of impedance. Besides, an indication of the changes in actual surface area may 2 serve the slight decrease in the discharge potential for NaCl at the end of the discharge test 3 (shown in Fig. 1a). On the contrary, as illustrated in Fig. 2c, the impedance of the anode after 4 discharge in solution with 5 mM InCl₃ shows an enhancing tendency with increasing discharge 5 time. The increased impedance is most likely caused by the progressive formation of a surface 6 film on the anode, which leads to positive shift of potential as shown in Fig. 1a. Nevertheless, 7 the impedances of Mg-0.15Ca in NaCl solution with 5 mM InCl₃ are always lower than that in 8 blank NaCl. Thus, the surface film formed in the electrolyte with 5 mM InCl₃ is less protective 9 than that formed in blank NaCl and induces less surface film-relevant overvoltage, resulting in a more negative discharge potential especially in the initial 10 h. 10

11

(Fig. 2)

The surface morphologies of the Mg-0.15Ca anode after discharge for varied periods in the 12 13 solution with 5 mM InCl₃ additive are presented in Fig. 3. Fig. 3(a-c) indicate that the surface 14 film formed after 24 h discharge is denser and more compact comparing to that after short time 15 discharge, which is in agreement with the EIS data in Fig. 2c. The elemental mapping for the 16 surface film formed after one-hour discharge (Fig. 3(d-g)) demonstrates some In(OH)₃ precipitates, occasionally found at the surface, while most of the surface is covered by 17 18 Mg(OH)₂. Moreover, as illustrated by the elemental mapping depicted in Fig. 3(h-k), the coverage of In(OH)₃ on the anode surface after 5 h discharge increases. After 24 h discharge, 19 20 the anode surface is almost fully covered by $In(OH)_3$ as shown in Fig. 3(1-o). The cross-21 sectional morphology and corresponding elemental mapping results exhibited in Fig. 3(p-s) 22 shown that the In element enriches in the outmost layer, elucidating the film is composed of 23 thin outer layer of mostly In(OH)₃ and thick inner layer of mainly Mg(OH)₂. The enhancement 24 of impedance value amid the discharge process in the electrolyte with InCl₃ is contributed by the growth of this mixed surface film and consequently results in the positive shift of discharge
 potential.

3

(Fig. 3)

The formation of the mixed surface film is attributed to the addition of $InCl_3$. As above mentioned, the initial pH of NaCl solution with 5 mM $InCl_3$ is 4.1 ± 0.1 , which is more acidic than the non-buffered blank NaCl electrolyte with initial pH 5.6 ± 0.1. The pH decrease after InCl₃ addition is related to the hydrolysis of In^{3+} ions as indicated by the following reactions and the hydrolysis constant of In^{3+} are found in the literature [48],

9
$$In^{3+} + H_2O = InOH^{2+} + H^+; \log K_1 = 10.0$$
 (6)

 $InOH^{2+} + H_2O = In(OH)_2^+ + H^+; \log K_2 = 10.18$ (7)

11
$$In(OH)_{2}^{+} + H_{2}O = In(OH)_{3(s)} + H^{+}; \log K_{3} = 9.42$$
 (8)

Moreover, the addition of InCl₃ is also capable to stabilize the pH of electrolyte even after 24 12 13 h discharge. The final pH of NaCl solution with 5 mM InCl₃ after 24 h discharging test is 4.3 \pm 0.1. According to the thermodynamic equilibrium diagram shown in Fig. 4, stable In(OH)₃ 14 15 precipitates form at pH above 4 in NaCl solution with 5 mM InCl₃, whereas stable Mg(OH)₂ precipitates from pH 10.3. The concentration of Mg²⁺ adopted for the thermodynamic 16 calculation is deduced from the weight loss of Mg-0.15Ca anode after 24 h discharge test in 17 the electrolyte with 5 mM InCl₃. As above mentioned, the final pH of NaCl solution with 5 18 19 mM InCl₃ is 4.3, which seems to be too acidic for the formation of stable Mg(OH)₂ precipitation presented in Fig. 3. However, the final pH is referred to the final pH of bulk electrolyte, which 20 21 is not representative for the local environment [35]. With the aim to clarify the influence of InCl₃ on the formation of discharge products film, the local pH on Mg-0.15Ca anode under 22 galvanic polarization is measured and illustrated in Fig. 5. 23

As presented in Fig. 5a, the local pH on Mg-0.15Ca anode in blank NaCl solution increases
 immediately after discharge and stabilizes at around 10.3. The increase of pH in blank NaCl
 solution is due to the cathodic reaction,

4

$$2H_2O + 2e^- = H_2 + 2OH^- \tag{9}$$

5 In NaCl solution with 1 mM InCl₃, the local pH close to the electrode surface also increases 6 rapidly within the initial 5 min from 4.3 to 9.7, which only shows marginal pH buffering effect 7 of 1 mM InCl₃ comparing to that in blank NaCl. By contrast, 5 mM InCl₃ addition efficiently 8 retards the increase of local pH in the region of 20 µm above Mg-0.15Ca anode, resulting in 9 the pH stabilization at 4.6 even after 150 min discharge. Fig. 5b shows the gradients of pH on 10 Mg-0.15Ca anode amid discharge, displaying the change of pH from 20 to 3000 µm above the anode surface. As presented in Fig. 5b, there is no significant difference between the local pH 11 and bulk pH in the blank NaCl solution, both of which are alkaline. By comparison, the bulk 12 13 pH of the InCl₃-containing electrolytes are both less than 5, which is consistent with the final bulk pH of InCl₃-containing electrolytes after 24 h half-cell discharge tests. However, the local 14 15 pH in the electrolyte with different concentrations of InCl₃ is distinctly different. In this region of 20 µm above Mg-0.15Ca anode, the local pH in the electrolyte with 1 mM InCl₃ solution is 16 9.7 whilst that in 5 mM InCl₃-containing electrolyte, i.e. 4.6, is only slightly higher than bulk 17 18 pH (4.4), indicating the addition of InCl₃ with different concentrations imparts remarkable 19 impact on the local environment of Mg-0.15Ca anode during discharge. The local pH (9.7) in 20 the electrolyte with 1 mM InCl₃ solution is close to that in blank NaCl solution (10.3) and, thus, 21 Mg-0.15Ca anode exhibits similar discharge behavior in these two electrolytes. In the electrolyte with 5 mM InCl₃, the concentration of In³⁺ decreases with the increase of discharge 22 time via the hydrolysis reactions (Eq. 6-8) and the precipitation reaction with OH⁻ generated by 23 24 cathodic reaction. Thus, the discharge potential of Mg-0.15Ca in the electrolyte with 5 mM 25 InCl₃ gradually shifts to a more positive value.

1 Fig.5c exhibits the evolution of surface condition of Mg-0.15Ca anode during local pH 2 measurements. After 20 min discharge, the products have already formed on the anode surface 3 in the electrolyte with 5 mM InCl₃, whereas the discharge products in blank NaCl and 1 mM 4 InCl₃-containing NaCl electrolyte cannot be visually observed. After 60 min discharge, 5 filiform-like corrosion starts on the anode surface in blank NaCl solution. The surface of Mg-0.15Ca in the electrolyte with 5 mM InCl₃ is completely covered by fluffy discharge products. 6 7 According to the local pH obtained from the region (4.6) and the equilibrium diagram presented 8 in Fig. 4, these fluffy discharge products are most likely to be In(OH)₃, demonstrating that the local environment in this region is strongly influenced by the hydrolysis reaction of In³⁺. Hence, 9 the precipitation of stable Mg(OH)₂ is less pronounced in this region. As indicted in Fig. 3a, 10 11 Mg(OH)₂ precipitation is the main component of the surface film on Mg-0.15Ca after 1 h 12 discharge, revealing the growth of Mg(OH)₂ film is underneath the porous In(OH)₃ layer. 13 Moreover, the structure of Mg(OH)₂ film shows less protectiveness due to the acidic environment introduced by the hydrolysis reaction of sufficient In³⁺. Thus, the discharge 14 potential of Mg-0.15Ca anode is improved by the addition InCl₃. Fig. 5d and 5e are presented 15 to show the distribution of local pH above Mg-0.15Ca anode in order to exclude the influence 16 17 of preferential localized corrosion, like the filiform-like corrosion happened in blank NaCl solution, on the results presented in Fig. 5a and 5b. 18

19

(Fig. 5)

20 **3.3 Self-corrosion and utilization efficiency**

Fig. 6 presents the evolved hydrogen volume of Mg-0.15Ca anode during discharge at 1 mA cm⁻² in the electrolyte with and without InCl₃. The real-time hydrogen evolution reflects the self-corrosion rate of anode amid discharge process. Apparently, the increment of InCl₃ concentration increases the self-corrosion of the Mg-0.15Ca anode. The addition of 1 mM InCl₃ suppresses the anode self-corrosion rate, while the addition of 10 mM InCl₃ results in a reverse

1 effect. The overall self-corrosion rate within the 24 h discharge in the electrolyte with 5 mM 2 InCl₃ additive is close to that in blank NaCl, in spite of one period with a higher self-corrosion 3 rate at the beginning. It is remarkable that addition of low concentration (1 mM) of InCl₃ is 4 able to decrease the self-corrosion rate of the Mg-0.15Ca anode, taking into consideration a 5 common sense that lowering solution pH leads to higher corrosion rates of Mg-based materials 6 at OCP condition [49-51]. Nevertheless, previous works have reported that the corrosion 7 behavior of Mg at OCP condition might differ from the self-corrosion under polarization (or 8 discharge) at varied current densities [9, 45], which is most probably because of the negative 9 difference effect (NDE) [47] commonly found on Mg and Mg alloys. The inhibiting effect of 10 1 mM InCl₃ on the self-corrosion of Mg-0.15Ca under polarization is in agreement with that 11 reported in the work of Gore et al.[45], which did not show relevant results regarding the effect 12 of higher InCl₃ concentration on Mg anode self-corrosion during discharge. In that work, the 13 authors proposed that the deposition of In(OH)₃/In₂O₃ on Mg might be the reason for the 14 unchanged cathodic kinetics of Mg as well as the inhibited self-corrosion during anodic 15 polarization of Mg in 0.1 M NaCl solution with 1 mM InCl₃. The provided results only show the existence of In species on Mg surface but the evolution of the In(OH)₃/In₂O₃ layer during 16 17 anodic polarization and the interrelated inhibition effect of In(OH)₃/In₂O₃ has not been investigated yet. 18

According to the results obtained from local pH measurements, the addition of 1 mM InCl₃ is not capable to significantly change the local pH of Mg-0.15Ca anode under polarization in our work, which may not largely accelerate the dissolution of anode during discharge. The addition of 5 mM InCl₃ efficiently restricts the increase of local pH at the initial stage of discharge, which also accelerates the self-corrosion rate of Mg-0.15Ca anode at the beginning. After 24 h discharge, an uniform In(OH)₃ outer layer is formed on Mg-0.15Ca anode in the electrolyte with 5 mM InCl₃ and, meanwhile, the self-corrosion rate slows down. It seems the 1 growth of this In(OH)₃ layer may be the vital origin for the self-corrosion inhibition effect of 2 InCl₃. However, the surface film formed in 5 mM InCl₃-containing electrolytes is always less 3 protective than that formed in blank NaCl solution according to the EIS results. Moreover, 4 there is no sign can be found in Fig. 2d that the In(OH)₃ layer leads to the formation of another 5 time constant. Therefore, it is hard to directly attribute the self-corrosion inhibition effect of InCl₃ to the deposition of In(OH)₃. Further understanding of the origin of NDE effect for Mg 6 7 and on the barrier / transport properties of the deposits is required to clarify the inhibition 8 mechanism of InCl₃.

9

(Fig. 6)

Interestingly, the change of utilization efficiency after adding InCl₃ (Fig. 1b) is not in 10 11 accordance with the induced alteration on real time self-corrosion rate (Fig. 6). The Mg-0.15Ca 12 anode in the solution with 5 mM InCl₃ shows a similar self-corrosion rate to that in blank NaCl 13 solution, but possesses a higher utilization efficiency, 56.8% versus 51.4%. By contrast, adding 14 10 mM InCl₃ leads to an increased self-corrosion rate but does not render big difference to the 15 utilization efficiency. This case must be related to the other form of self-corrosion, i.e. chunk 16 effect, which is not fully included in the real-time hydrogen evolution. As demonstrated by 17 Deng and co-workers [9], chunk effect, which refers to the detachment of secondary phases 18 and undissolved matrix from anode substrate due to non-uniform dissolution, also causes large loss of anode utilization efficiency in some cases. Assuming hydrogen evolution is the 19 20 dominating form of anode self-corrosion, the theoretical utilization efficiency can be calculated 21 according to the real-time generation rate of hydrogen as displayed in Fig. 6 via the following equation. 22

23
$$\eta_{theo} = \frac{m_{dis}}{m_{dis} + m_H} \tag{10}$$

Where m_{dis} is the mass loss of anode due to applied discharge current, while m_H is the mass loss associated with cathodic hydrogen evolution reaction. Accordingly, the calculated theoretical efficiency is 60.6 % in blank NaCl electrolyte and 61.2% in the electrolyte with 5 mM InCl₃. Thus, the contribution of chunk effect to the efficiency loss could be roughly estimated via comparing the actual and theoretical efficiency, indicating that of 9.2% and 4.4% for the blank solution and 5 mM InCl₃-containing solution, respectively. Anode efficiency loss because of chunk effect is reduced via InCl₃ addition.

- Fig. 7 shows the surface morphology of the Mg-0.15Ca anode after discharge and removing discharge products. The anode surface after discharging in blank NaCl solution is uneven with large cavities (Fig. 7a). After 1 mM InCl₃ addition, the anode surface is relatively uniform, but shows some small holes (Fig. 7b). Such holes in smaller size are also found on the flat anode surface after discharging in the solution with 5 mM InCl₃ (Fig. 7c). By contrast, a generally flat and uniform surface without visible pits appears regarding 10 mM InCl₃ (Fig. 7d).
- 12

(Fig. 7)

Fig. 8 displays the 3D reconstruction and corresponding depth profile for the anode 13 14 topography after discharging after removal of discharge products. Obviously, flat anode surfaces with smaller roughness are obtained after using InCl₃ as an additive. Besides, the 15 surface roughness decreases with the increment of InCl₃ concentration as shown in Fig. 8i. The 16 17 results elucidate that InCl₃, as an additive, possesses the capability of homogenizing the dissolution of the Mg-0.15Ca anode, thus contributing to reduced chunk effect. With 10 mM 18 19 InCl₃, the acceleration on hydrogen evolution during discharge is compensated by reduction of 20 chunk effect, leading to similar utilization efficiency and capacity to those in blank electrolyte.

21

(Fig. 8)

22 **3.4 Mg-air battery testing**

In the half-cell discharge testing, the addition of 10 mM InCl₃ significantly improves the discharge potential of Mg-0.15Ca alloy and maintains the effectiveness for 24 h discharging

1 process. Besides, no negative effect is imparted to the anode utilization efficiency. Hence, we 2 propose that 10 mM InCl₃ is a suitable electrolyte additive for aqueous Mg batteries. In this 3 context, testing of aqueous Mg-air battery was done to evaluate its feasibility in a fully 4 assembled battery system. Fig. 9(a-c) present the discharge curves of Mg-air battery in the 5 electrolyte with and without 10 mM InCl₃ under different current densities. The addition of InCl₃ significantly improves the cell voltage in all cases. Amid discharge at 1 mA cm⁻², adding 6 InCl₃ increases the cell voltage by 220 mV, namely, from 1.52 V to 1.74 V. During the initial 7 5 h discharging test at 5 mA cm⁻², the voltage of Mg-air battery in the electrolyte containing 8 InCl₃ is 1.42 V, whereas the cell voltage in blank NaCl solution is 1.37 V. Nevertheless, the 9 enhancement of cell voltage induced by InCl3 weakens after 8 h discharge and stabilized at 10 11 1.39 V. The addition of 10 mM InCl₃ also improves the cell voltage under 10 mA cm⁻², which 12 is 50 mV higher than that in reference test. Fig. 9d summarizes the improvement of discharge 13 performance by adopting 10 mM InCl₃ as electrolyte additives. As illustrated in Fig. 9d, the most significant enhancement regarding the specific energy is obtained under 1 mA cm⁻². With 14 15 the increase of current density, the enhancement of discharge performance is decreasing. As displayed in Fig. 9e, a large amount of discharge products have precipitated and blocked the 16 17 active surface of air cathode after discharging test, which may also give rise to the drop of cell voltage in the discharging test with high current density. As indicated in the XRD diffraction 18 19 pattern, the precipitates on the air cathode are the mixed In(OH)₃ and Mg(OH)₂, which 20 preferentially form on the air cathode because the cathodic reaction of Mg-air battery generates a large amount of OH⁻. This problem can be addressed by applying selective permeable 21 membrane, which should be considered in Mg-air battery configuration design for future works. 22

23

(Fig. 9)

1 4. Conclusions

In this work, we evaluate the feasibility of InCl₃ as an electrolyte additive for aqueous Mg batteries. The half-cell discharge behavior, surface state evolution, self-corrosion rate during discharge of Mg-0.15 wt.% Ca anode and fully assembled aqueous Mg-air battery performance are determined in 3.5 wt.% NaCl solution with and without InCl₃. Following conclusions are drawn:

(1) Addition of InCl₃ improves the discharge potential of the anode. However, the enhancement
weakens with discharge time. Higher InCl₃ concentration (10 mM) enables the anode with
significantly more negative discharge potential and the enhancement lasts for a longer term,
because the addition of In³⁺ is capable of retarding electrolyte alkalization during discharge
due to its hydrolysis reaction, which leads to better discharge activity and less film-relevant
potential drop.

(2) Local measurement reveals that the pH buffering effect induced by the addition of InCl₃
depends on its concentration. Addition of sufficient InCl₃ is able to hinder the increase of local
pH close to the interface amid discharge. Nevertheless, 1 mM InCl₃ addition only shows pH
buffering effect for the bulk environment, but the local pH is close to that in blank NaCl,
resulting in similar discharge potential.

18 (3) 1 mM InCl₃ addition significantly decrease the self-corrosion rate of the Mg-0.15Ca anode 19 amid discharge at 1 mA cm⁻². However, the self-corrosion rate is accelerated with the 20 increment of InCl₃ concentration from 0.26 ml cm⁻² h⁻¹ (1 mM) to 0.32 ml cm⁻² h⁻¹ (10 mM).

(4) InCl₃ at a low concentration enhances the anode utilization efficiency, e.g. from ~51% to
~57% after adding 1 mM InCl₃. Addition of 10 mM InCl₃ homogenizes the anode dissolution,
reducing anodic efficiency loss caused by chunk effect and maintaining the anode utilization
efficiency to 52%.

2	
	Mg-air battery, especially at lower current densities. The highest cell voltage and specific
3	energy of aqueous Mg-air battery is achieved by adding 10 mM $InCl_3$ to 1.74 V and 2.26
4	kWh/kg (at 1 mA cm ⁻²). The improvement could be further enhanced via combination with
5	battery configuration/cell design.
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11	Acknowledgement
12	The authors are grateful for the technical support of Mr. Gert Wiese, Mr. Ulrich Burmester
13	and Mr. Volker Heitmann. Ms. Linqian Wang, Mr. Min Deng and Mr. Cheng Wang thank
14	China Scholarship Council for the award of fellowship and funding (No. 201706370183, No.
15	201606370031, and No. 201806310128. Dr. Darya Snihirova acknowledges SeaMag project
16	for financial support (MarTera ERA-NET cofund).
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- 1 Table:
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 Table 1 Chemical composition of the produced Mg-0.15Ca alloy anode (wt.%).

	Ca	Fe	Ni	Cu	Si	Al	Zn	Mg
Mg-0.15Ca	0.15	0.0014	0.0002	0.0002	0.0056	0.0021	0.0020	Bal.

1 Figure captions

2 **Fig. 1** Half-cell discharge performance of Mg-0.15Ca anode at 1 mA cm⁻² in 3.5 wt.% NaCl

3 with and without InCl₃: (a) discharge curves and (b) utilization efficiency and discharge

4 capacity of Mg-0.15Ca.

Fig. 2 EIS plots of Mg-0.15Ca anode measured after discharge at 1 mA cm⁻² for different times
in 3.5 wt.% NaCl solution (a) and (b) blank; (c) and (d) with 5 mM InCl₃.

Fig. 3 Surface and cross-sectional morphologies of Mg-0.15Ca anode after discharge at 1 mA
cm⁻² in 3.5 wt.% NaCl solution with 5 mM InCl₃. Surface after (a)1 h; (b) 5 h; (c) 24 h.
Elemental mapping for the surface after (d-g) 1 h; (h-k) 5 h; (l-o) 24 h. Cross section and

- 10 corresponding elemental mapping after 24 h (p-s).
- Fig. 4 Thermodynamic calculation of the equilibrium composition of relevant species in 3.5
 wt.% NaCl solution with 5 mM In³⁺ and 2 mM Mg²⁺ via Hydra-Medusa program.

13 Fig. 5 (a) local pH above Mg-0.15Ca anode (20 μm); (b) vertical distribution of pH from Mg-

14 0.15Ca anode surface to bulk environment; (c) the surface evolution of Mg-0.15Ca anode; and

15 (d) horizontal distribution of local pH above Mg-0.15Ca anode (50 μ m) at 1 mA cm⁻² in blank

16 NaCl and NaCl solution with 5 mM InCl₃

Fig. 6 Real-time hydrogen evolution of Mg-0.15Ca anode during discharge at 1 mA cm⁻² in
3.5 wt.% NaCl solution with InCl₃ of different concentration.

Fig. 7 Surface morphologies of Mg-0.15Ca anode after discharge at 1 mA cm⁻² for 24 h and
removal of discharge products in 3.5 wt.% NaCl solution with InCl₃: (a) blank; (b) 1 mM; (c)
5 mM; (d) 10 mM.

Fig. 8 3D reconstruction and corresponding depth file for the Mg-0.15Ca anode topography without discharge products after discharge at 1 mA cm⁻² for 24 h in 3.5 wt.% NaCl solution with InCl₃ of different concentration: (a, b) blank; (c, d) 1 mM; (e, f) 5 mM; (g, h) 10 mM; and

(i) surface roughness of Mg-0.15Ca anode in 3.5 wt.% NaCl solution with InCl₃ of different
concentration.

3	Fig. 9 Discharge curves of Mg-air battery with Mg-0.15Ca anode in 3.5 wt.% NaCl solution
4	with and without 10 mM InCl ₃ at (a) 1 mA cm ⁻² , (b) 5 mA cm ⁻² , and (c) 10 mA cm ⁻² ; (d)
5	specific energy and average cell voltage of Mg-air battery with Mg-0.15Ca anode in 3.5 wt.%
6	NaCl solution with and without 10 mM InCl ₃ ; (e) optical image and XRD diffraction pattern
7	of the precipitation on air cathode after discharge.
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Figures

Fig. 1

































