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Float-charging protocol in rechargeable Zn–MnO_2 batteries: Unraveling the key role of Mn^{2+} additives in preventing spontaneous pH changes

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A B S T R A C T

Aqueous rechargeable Zn–MnO_2 batteries have been attracting increasing interest in recent years due to their relatively high energy density, non-toxicity, non-flammability, and low-cost. However, the battery chemistry still faces several challenges limiting the performance of some key performance indicators and preventing its commercial deployment. Among these, cycle stability and lifespan are important, especially for stationary energy applications, and require improvement. In this work, a spontaneous reaction between Zn metal and electrolytes evolving hydrogen and Zn ions is shown to drive the electrolyte pH towards alkaline conditions, which in turn hinders the reversible electrochemical reactions at both positive and negative electrodes. Proton release during the oxidation of a Mn^{2+} additive and promotion of the oxygen evolution reaction (OER) at the positive electrode by implementing a float-charging protocol (constant voltage at the end of the charging process) is proposed as a simple strategy to restore the initial pH. Using a pH indicator dissolved in the electrolyte and assembling the electrochemical cell in a spectrophotometer cuvette, the effect of floating voltage is evaluated in operando, allowing optimization of the floating voltage to enable the electrolyte pH to remain stable.

1. Introduction

Energy storage systems have become key elements in the transition to a more sustainable energy model [1] by (i) buffering energy to match the demand and intermittent production of energy from renewable sources, and (ii) powering electric vehicles. Batteries, and Li-ion batteries (LIBs) in particular, are considered an excellent compromise due to their relatively high energy density, cycle stability, energy efficiency and cost. On the other hand, LIBs still face important challenges, in particular safety issues related to the use of flammable organic solvents and the availability of critical raw materials (e.g. Li, Co) [2,3]. To overcome these challenges, much effort has been devoted to the development of battery chemistries based on abundant elements and aqueous electrolytes [4]. Rechargeable zinc-ion batteries are an attractive alternative owing to the intrinsic characteristics of Zn as a negative electrode material: high specific capacity (820 $mAh \cdot g^{-1}$), relatively cathodic redox potential (-0.76 V vs Standard Hydrogen Electrode at neutral pH), non-toxicity, non-flammability and low cost due to its high abundance, as well as the well-known commercial processes for production and recycling [5–7].

Zinc–manganese oxide batteries are commercially available as alkaline primary batteries due to their low cost and specific capacity (100–300 mAh g^{-1} depending on the structure). Therefore, the development of rechargeable Zn–MnO_2 batteries has been the focus of much attention in the last decade as a low-cost and safe energy storage solution [8]. This rechargeable battery was reported for the first time using $ZnSO_4$ as a mildly acidic electrolyte [5,9,10] instead of the alkaline media used in non-rechargeable commercial Zn–MnO_2 batteries. In a neutral or mildly acidic electrolyte, Zn is reversibly plated and stripped on the negative electrode while the charge storage mechanism on the positive electrode material is still under debate: possible Zn^{2+} intercalation [11,12] and/or Mn electrodissolution/electroplating [13–16]. In any case, insulating layers have been identified on the electrode surfaces during the discharge process [17] e.g. $Zn_{12}(CF_3SO_3)_9(OH)_{15}\cdot nH_2O$ [18], $Zn_4ClO_4(OH)_7$ [19], or $Zn_4SO_4(OH)_6\cdot nH_2O$ (ZHS) [20–22] in $Zn(CF_3SO_3)_2$, $ZnSO_4$ and $Zn(ClO_4)_2$ electrolytes, respectively. These compounds are usually generated when the solution becomes alkaline [23]. Thus, changes in the electrolyte pH towards alkaline values must be avoided if the electrochemical reactions in Zn–MnO_2 batteries are to remain reversible. Since charge storage in MnO_2 involves the uptake and

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release of protons, evolution of the electrolyte pH during the charge/discharge process has been studied [24–26]. Surprisingly, changes in the electrolyte pH due to a possible spontaneous reaction between Zn metal and protons at a neutral pH, which should thermodynamically occur according to the Pourbaix diagram for Zn at a mildly acidic pH [8], have not been investigated. This reaction is very relevant considering that spontaneous oxidation of Zn metal would consume protons, leading to an increase in the electrolyte pH.

Herein, evolution of the electrolyte pH over time is investigated by dissolving a pH indicator in the electrolyte and assembling an electrochemical cell in a spectrophotometer cuvette. This setup not only allows for confirmation of pH drift towards alkaline values, but also clearly reveals that changes in the electrolyte pH originate at the Zn metal electrode. Based on this, a simple charging protocol is proposed to keep the pH value of the electrolyte constant, which consists in implementing a float charging step (constant voltage) at the end of the charge process. By holding the voltage at the fully charged state, oxidation of Mn^{2+} dissolved in the electrolyte and the oxygen evolution reaction are promoted at the positive electrode, releasing protons and compensating for the pH change induced at the negative electrode by spontaneous reaction between Zn and protons.

2. Materials and methods

$MnSO_4$ H_2O (≥99 %, Sigma Aldrich), $ZnSO_4$ $7H_2O$ (≥99.5 %, Sigma Aldrich), zinc Foil (99.98 %, Alfa Aesar), NaCl (99 %, Alfa Aesar), KCl (99 %, Alfa Aesar), LiCl (99 %, Alfa Aesar), and Bromocresol Green (Panreac) were used as received. A UV–vis cuvette was used as an open electrochemical cell, and expanded graphite (Sigracet TF6) was used as the substrate for electrodeposition of MnO_2. An aqueous solution of 2 M $ZnSO_4$ + 0.1 M $MnSO_4$ was used as the electrolyte in this work, with a measured pH of 3.74. Bromocresol Green (Panreac) was added to the electrolyte as a pH indicator. 0.04 g Bromocresol was dissolved in 100 mL of 20:80 (ethanol:water) solution. Then, one droplet of this solution was added to the 3 mL electrolyte. Note that, in the long-term experiment, the indicator was added right at the end of the measurement (300th cycle) to avoid any interference from the indicator.

MnO_2 electrodes were fabricated by electrodeposition. The expanded graphite (working electrode) was introduced into a solution of 0.5 M $KMnO_4$ (Panreac, 98.5 %) for the reduction according to eqn. (1). A platinum wire and Ag/AgCl were used as the counter and reference electrodes, respectively [27].

$$MnO_4^- + 2H_2O + 3\,e^- \rightarrow MnO_2 + 4OH^- \tag{1}$$

MnO_2 was electrodeposited on rectangles (1 × 5 cm) immersed in the electrolyte to a depth of 3 cm, leaving the other 2 cm for the electrical connection. The active area is therefore 3 cm^2 (3 mL of volume). The mass loading is estimated to be ca. 0.24 $mg_{MnO2}\cdot cm^{-2}$.

An AUTOLAB PGSTAT 12 was used for all the electrochemical measurements. For the cyclability test, a constant current (both charge and discharge processes) of 1 mA cm^{-2} was applied, implementing, where indicated, the float-charging step.

3. Results and discussion

3.1. Role of the electrolyte pH in zinc–manganese dioxide batteries

The electrolyte pH plays a critical role in the reversibility of Zn–MnO2 batteries since insulating products with poor electrochemical reversibility are obtained in alkaline media. Lee et al. studied the changes in the electrolyte pH associated with the charge storage mechanism of MnO_2 during charge and discharge [25]. This work confirmed the evolution of the electrolyte pH during the charge and discharge process: "During discharge, unstable trivalent manganese deprotonates and dissolves into the electrolyte resulting in a gradual increase in the pH value of the electrolyte. This triggers precipitation of zinc hydroxide sulfate from the electrolyte on the electrode surface. During charging, the pH value of the electrolyte reverts to being acidic as a result of manganese recombination on the cathode that causes zinc hydroxide sulfate to re-dissolve into the electrolyte". While this was not analyzed in detail, their results also showed that the overall pH value of the electrolyte was becoming alkaline over time, that is, there was an accumulated increase in the pH value during subsequent cycles. This observation motivated us to assemble an electrochemical cell in a spectrophotometer cuvette using MnO_2 film electrodeposited on expanded graphite and Zn foil as positive and negative electrodes, respectively, and dissolving a pH indicator (Bromocresol Green) in the electrolyte (Fig. 1a). It should be noted that a similar setup was reported by Bischoff et al. [26], which was shown to be highly suitable for this type of task. However, this previous study focused on the evolution of the electrolyte pH during the charge–discharge process, overlooking the spontaneous reaction between Zn metal and water. In our work, since the color range of Bromocresol Green as an indicator is: yellow ($pH < 3$), green ($3 < pH < 5$), and blue ($pH > 5$), the electrolyte ($pH \approx 4$–4.5) is initially green (Fig. 1b).

While a number of reactions driven by the charge/discharge processes can induce changes in the pH value [24–26], any spontaneous changes should first be assessed. Therefore, the cell was left at open circuit voltage (OCV) for 22 h (Fig. 2). Without the application of an external bias, the color of the electrolyte changed from green to blue after 22 h, indicating that the electrolyte is spontaneously turning alkaline. This change is attributed to the reaction between Zn metal and protons from the electrolyte giving rise to Zn ions and hydrogen, as illustrated in the scheme shown in Fig. 2. A closer look at the photo of the initial state, in which the electrolyte is green, reveals that the electrolyte near the Zn electrode (left-hand electrode) forms a thin blue layer. This indicates that the origin of the changes in the electrolyte pH is the spontaneous reaction at the Zn metal electrode. Additional experiments using Zn powder (Section 1 in the supporting information) clearly illustrate that the kinetics of the spontaneous reaction are not as slow as one might assume. The mass loss of the Zn foil over three days was also measured to estimate quantitatively the change in pH over time for Zn foil under static conditions, confirming that the spontaneous reaction between water and Zn metal is an important issue for long-term operation.

Since the reduction of water (hydrogen evolution reaction) at the negative electrode drives the change in the electrolyte pH, the opposite reaction taking place at the positive electrode could potentially compensate for these changes in the pH value. Therefore, we explored the promotion of the oxygen evolution reaction at the positive electrode as a solution to restore the pH value by holding the voltage at the end of the charge process. This strategy is based on the floating protocols employed in lead-acid battery technology [28], which have not yet been explored for Zn–MnO_2 to control changes in the electrolyte pH and prolong cycle life. Fig. 3 shows the influence of the value of the float voltage on the electrolyte pH. A cell was left at OCV for 22 h, spontaneously turning blue (alkaline). Then, different constant voltages (1.7 V, 1.8 V, 1.9 V and 2.0 V) were applied. The pH of the electrolyte near the positive electrode (right-hand electrode in Fig. 3) turned yellow, indicating acidification. The higher the applied voltage; the thicker the acid layer. This set of photos reveals that the float-charging protocol can be used as an effective strategy to acidify the electrolyte.

The presence of Mn^{2+} dissolved in the electrolyte was originally thought to suppress dissolution of MnO_2 during cycling [20]. Later on, it was reported to provide additional capacity, since Mn^{2+} can be electrodeposited [13–16,[29]. As oxidation of Mn^{2+} to MnO_2 involves the release of H^+ (eqn. (2)), oxidation of a Mn^{2+} additive during the float-charging step can also contribute to the acidification of the electrolyte. Experiments described in Section S2 of the supporting information reveal that approximately 80% of the charge consumed when a constant voltage of 1.8 V is applied for 1 h can be attributed to the oxidation of Mn^{2+}. Thus, both the OER and the oxidation of Mn^{2+} are responsible for

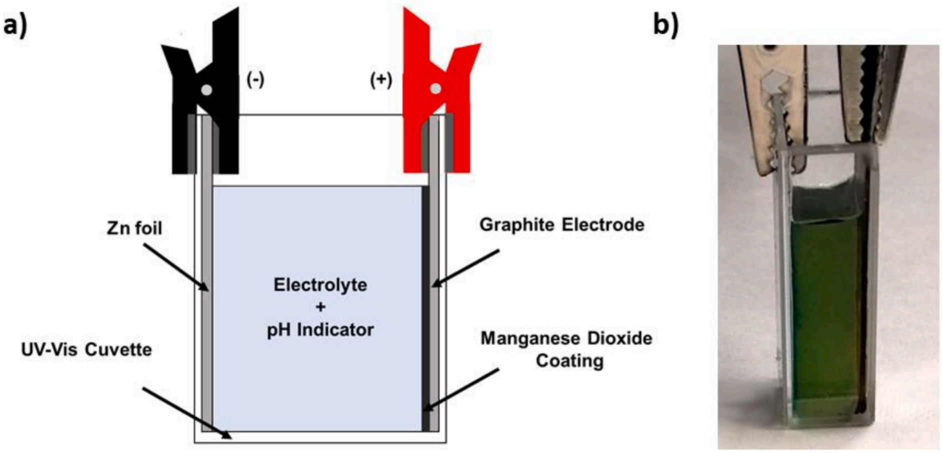

Fig. 1. (a) Schematic illustration of the Zn–MnO_2 cell assembled in a UV–vis cuvette. (b) Photo of the cell filled with electrolyte (2 M $ZnSO_4$ + 0.1 M $MnSO_4$) containing the pH indicator. The green color indicates that the pH value is between 3 and 5. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

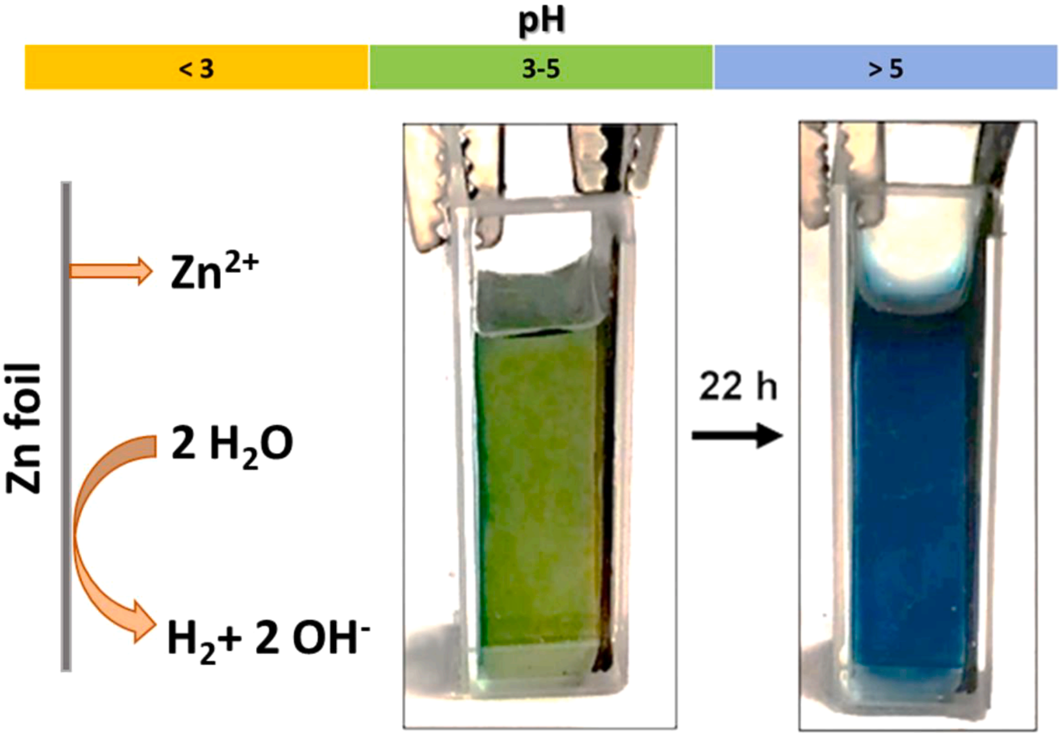

Fig. 2. Spontaneous evolution of electrolyte pH without the application of an external bias (2 M $ZnSO_4$ + 0.1 M $MnSO_4$ containing a pH indicator).

the regulation of the pH value during the float-charging step. Indeed, our estimates indicate that oxidation of Mn^{2+} is the main contributor, revealing the previously unknown key role of Mn^{2+} additives in cycle stability. However, the amount of Mn^{2+} is limited, so that its depletion may eventually prevent correction of the spontaneous pH drift. Using the corrosion rate determined for a Zn foil (Section 1 in the supporting information), one can make a rough estimate of the amount of Mn^{2+} required to correct the pH value in the long term. According to our estimations (Section 3 in the supporting information) 1 mM Mn^{2+} would be sufficient to maintain the pH value of a volume of 10 μL cm^{-2} of electrolyte. Thus, the concentration of Mn^{2+} most often reported in literature (0.1 M) should be more than enough for several years.

$$Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2\,e^- \qquad (2)$$

The float-charging protocol should be able to compensate for the changes in the electrolyte pH originating at the negative electrode and restore the initial pH value. To assess this, the electrolyte pH was evaluated after different float voltages had been applied for 2 h (Fig. 4). When a constant voltage of 2.0 V was applied for 2 h, the electrolyte turned acidic, as indicated by the color of the electrolyte (yellow indicates pH < 3). The same result was obtained for a float voltage of 1.9 V. On the other hand, a constant voltage of 1.7 V applied for 2 h was not able to completely restore the initial pH value, as indicated by the color of the electrolyte (turquoise blue indicates a pH close to but above 5). Only when a constant voltage of 1.8 V was applied to the cell was the electrolyte pH restored, as confirmed by the color of the electrolyte (green indicates a pH between 3 and 5). According to these results, the application of a float-charging protocol that consists in holding the voltage at 1.8 V at the end of the charge process should lead to improved

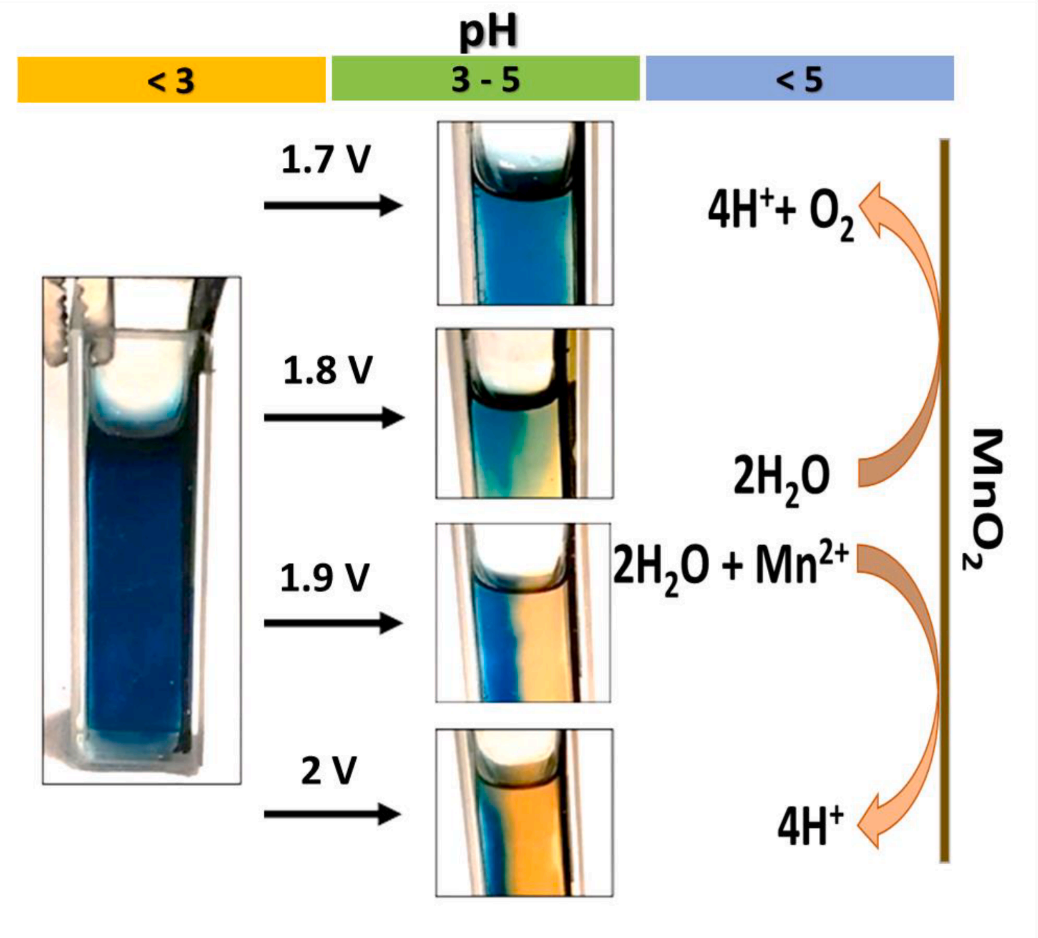

Fig. 3. Pictures of the cuvette cell after open circuit voltage (left) and when a constant voltage of 1.7 V, 1.8 V, 1.9 V or 2.0 V was applied to the cell for 2 h. The Zn foil is located at the left and the MnO_2 electrode at the right-hand side of the cuvette. Right: scheme of the electrochemical reaction taking place at the positive electrode. The electrolyte was 2 M $ZnSO_4$ + 0.1 M $MnSO_4$ containing a pH indicator.

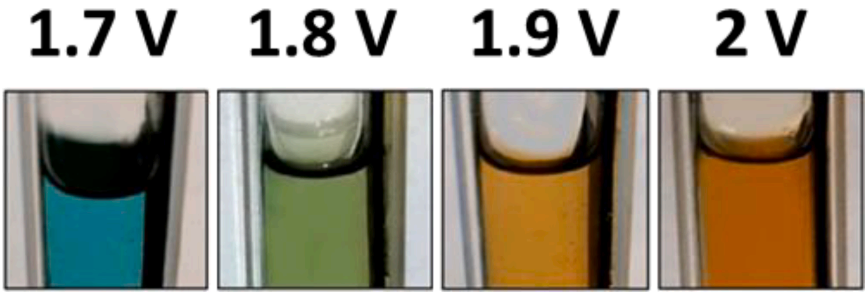

Fig. 4. Photos of the electrolyte after a float voltage of 1.7 V, 1.8 V, 1.9 V or 2.0 V had been applied for 2 h. The electrolyte was 2 M $ZnSO_4$ + 0.1 M $MnSO_4$ containing a pH indicator.

electrochemical performance.

3.2. Preventing pH drift via float-charging protocols in Zn–MnO_2 batteries

The evolution of the electrolyte pH indicates that the electrolyte is spontaneously changing towards alkaline values, while the application of a constant voltage at the end of the charge process can be used to restore the initial pH value. Thus, this finding should translate into a stable pH value during cycling. To explore this, a cuvette electrochemical cell was galvanostatically charged and discharged under float-charging protocols consisting in holding the voltage at 1.8 V for 15 min at the end of the charge step (Fig. 5). In this figure, photos of (i) the initial electrolyte and (ii) a cell left at the open circuit voltage for 22 h are included to illustrate the timescale of the experiment, since a spontaneous drift towards alkaline values was already observed after 22 h. Fig. 5 shows the evolution of the specific charge capacity upon cycling when the float-charging protocol was applied (a cut-off voltage of 1.7 V was held for 15 min at the end of the charge step). A slight but steady increase in specific capacity was observed. This behavior has been reported previously and is associated with the electrodeposition of Mn^{2+} [29], which is present in the electrolyte in the form of $MnSO_4$ as a standard additive in most reported Zn–MnO_2 batteries. According to eqn. (2), electrodeposition of additional MnO_2 from Mn^{2+} in the electrolyte leads to acidification of the media, and is the main source of

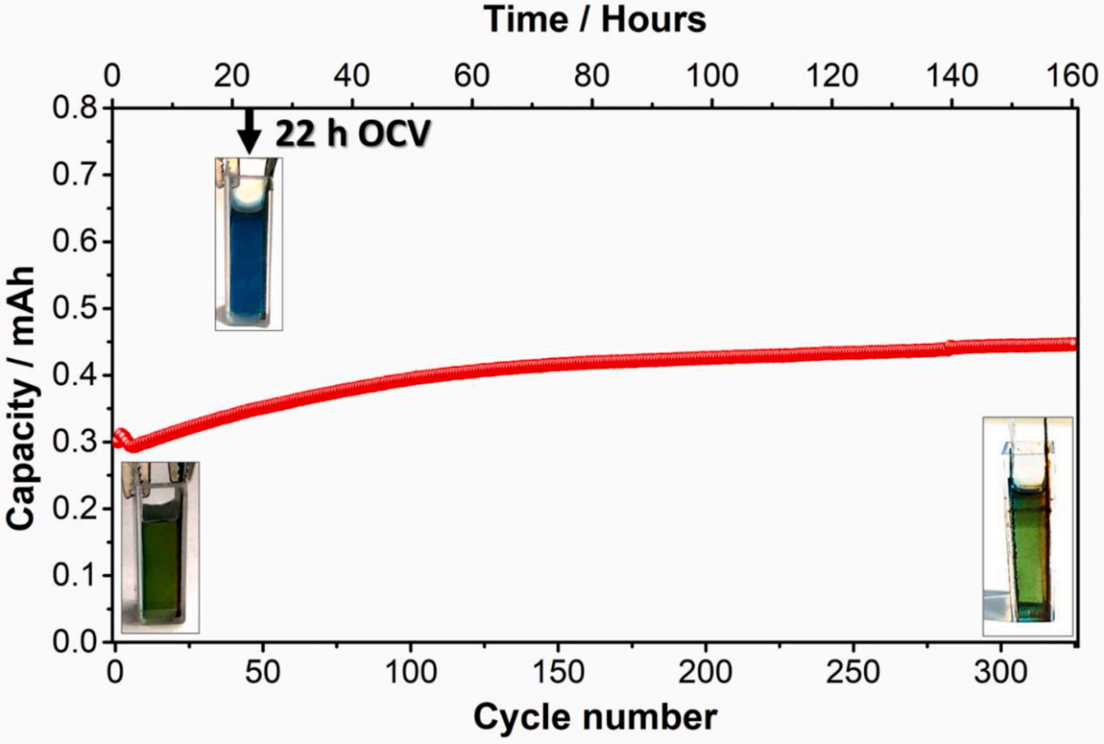

Fig. 5. Evolution of the charge capacity when a float-charging protocol is applied (1.8 V for 15 min). Inset: photos showing the initial color of the electrolyte; after 22 h at open circuit voltage (spontaneous drift towards alkaline values); and after 300 cycles implementing the float-charging protocol. The total duration of the experiment was > 160 h. A current density of 1 mA cm-^{2} was applied to implement a float-charging step of 1.8 V for 15 min at the end of the charge process. The electrolyte was 2 M $ZnSO_4$ + 0.1 M $MnSO_4$ containing a pH indicator.

protons to correct the spontaneous drift of the pH towards alkaline values. Indeed, the green color of the electrolyte after 300 cycles and > 160 h reveals that the implementation of a constant voltage step at the end of the charge process effectively prevents changes of pH towards alkaline values. Note that (i) the cell was cycled in the absence of indicator, which was added right at the end to avoid interference during cycling, and (ii) the duration of the experiment was 160 h, which is relevant for the timescale of Zn corrosion. Additional data from these experiments, i.e. coulombic efficiency and voltage profiles, are provided in Section 4 of the supporting information. Since accumulation of MnO_2 from the Mn^{2+} present in the electrolyte has been revealed as the main contributor, the measured coulombic efficiencies of ca. 100% are reasonable since the additional electrodeposited MnO_2 from Mn^{2+} contributes to the discharge process.

4. Conclusions

It is shown that the pH of the electrolyte in rechargeable Zn–MnO_2 batteries evolves spontaneously towards alkaline values due to the reaction between Zn metal and protons. This is an intrinsic issue related to the use of metal Zn and an aqueous electrolyte with a neutral or mildly acidic pH. Materials science research on the development of an artificial solid electrolyte interphase could prevent this, as the SEI prevents a spontaneous reaction between organic electrolytes and Li metal. Alternatively, a simpler approach that was explored and demonstrated to be useful in this work is the implementation of float-charging protocols for Zn–MnO_2 batteries, in which a constant voltage is held at the end of the charge process. In a spectrophotometer cuvette, a pH indicator was dissolved in the electrolyte of a cell containing Zn foil and MnO_2 previously electrodeposited on expanded graphite. In this cell, several charging protocols were studied, showing that the oxidation of the Mn^{2+} additive dissolved in the electrolyte and the occurrence of the oxygen evolution reaction (OER) controlled by the applied charging protocol are able to acidify the electrolyte. The use of this cell revealed the role of the cut-off voltage and float voltage in the change in the electrolyte pH. Intermediate values for the float voltage (e.g. 1.8 V) gave rise to the best results as higher values led to acidification of the electrolyte while lower values were not able to restore the initial pH value. Our estimates indicate that the amount of Mn^{2+} most often used in the literature (0.1 M) should be sufficient to correct the pH value for several years. Experiments in cycle stability using different charging protocols confirmed these findings, as the best cyclability was obtained when a cut-off voltage and float voltage of 1.8 V were applied. In any case, oxidation of Mn^{2+} and promotion of the OER taking place during the float-voltage protocol also address losses of Zn metal due to spontaneous corrosion, since Zn deposition should occur during application of the float voltage (if the HER takes place, the pH value will not be restored). Consumption of water should be small considering the amount of Mn^{2+} required for long-term operation (1 mM Mn^{2+} →4 mM H_2O (72 m g_{H2O} L^{-1})) and the fact that the oxygen released during application of the float voltage is expected to recombine with hydrogen from the Zn corrosion.

CRediT authorship contribution statement

Daniel Perez-Antolin: Methodology, Investigation, Visualization, Writing – original draft. **Inés Sáez-Bernal:** Investigation. **Alvaro Colina:** Supervision. **Edgar Ventosa:** Conceptualization, Methodology, Writing – review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.elecom.2022.107271.

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