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# Layered double hydroxides as a suitable substrate to improve the efficiency of Zn anode in neutral pH Zn-ion batteries

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ABSTRACT

Recently, neutral pH zinc-ion batteries (ZIBs) have received an increasing attention as a low cost and eco-friendly alternative to lithium-ion batteries. At variance with previous publications, we focused on the improvement of the zinc negative electrode in this work. By addition of layered double hydroxides to the preparation of the negative electrode, it was possible to increase the efficiency of zinc electro-deposition from 85% to 98%. This improvement was related to the elimination of a potential drop during the $Zn^{2+}$ reduction step, avoiding the formation of $H_2$ at the beginning of the discharging step.



## 1. Introduction

Currently lithium-ion batteries (LIBs) dominate the battery market with 37% of the total production. Its broad penetration as power sources for various portable devices, such mobile phones and laptops, is due to their good cycling performances and high energy densities [1]. However, LIBs are not an adequate technology as stationary energy storage systems to overcome the drawbacks associated with storage and use of renewable energy sources because of crucial issues related to safety, eco-friendliness, and the high cost. Recently, batteries based on abundant polyvalent cations, such as $Mg^{2+}$, $Zn^{2+}$, and $Al^{3+}$, have been studied as an alternative to LIBs for large scale electrochemical energy storage systems [2–5]. Among them, aqueous zinc-ion batteries (ZIBs) are considered as one of the best candidates for stationary applications since these devices are based on relatively abundant and cheap elements: a metallic zinc negative electrode, an aqueous $ZnSO_4$ or $ZnCl_2$ electrolyte, and an intercalating positive electrode. Different materials have been proposed as a zinc-intercalating active components of the positive electrode. $Na_{0.95}MnO_2$ [6], $MnO_2$-supported CNT nanocomposites [7], α-$MnO_2$ [8], and δ-$MnO_2$ nanoflake cells deliver a specific charge between 40 and 250 mAh $g^{-1}$ with an average discharge potential of 1.5 V [9]. The intercalation mechanism of zinc ions into α-$MnO_2$ and δ-$MnO_2$ has been recently studied by the use of in situ X-ray measurements [10,11]. CuHCF and ZnHCF Prussian Blue derivates have also been used as zinc-intercalating active materials with an operating voltage of 1.7 V and specific charge retention of 96% (CuHCF) and 76% (ZnHCF) after 100 cycles [12,13]. Another possibility is the employment of electrolytes containing a mixture of $Li^+$ and $Zn^{2+}$ cations, which permits the utilization of $LiFePO_4$ and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ as cathode material supplying a specific charge close to 120 mAh $g^{-1}$ and a potential of 1.15 V and 1.65 V, respectively [14,15]. While the active materials at the positive electrode have been the subject of several studies, the oxidation/reduction of zinc at the negative electrode as well as its influence on the electrochemical performance of these ZIBs has not been investigated in detail. To the best of our knowledge, just Kang et al. [16] analyzed the improvement on the specific charge retention of α-$MnO_2$–Zn battery by the addition of activated carbon in the zinc anode. However, the use of two electrode configuration cell hinders the possibility of identifying the effect of this additive on the potential profile of the zinc during the battery cycling. Therefore, it is not possible to discriminate with which electrode the specific charge losses were associated. Recently, our group published a work on the CuHCF-Zn battery [12], in which the potential profile of the zinc negative electrode was monitored together with the potential profile of the CuHCF-based positive electrode. From the analysis of the data, we could eventually observe that the increment of the roughness in the zinc electrode upon cycling was inducing a decrease of the $H_2$ evolution and dendrites formation. On the other hand, the layered double hydroxides (LDHs), or the so-called hydrotalcite-like compounds with a general formula $[M^{II}_{1-x}M^{III}_x(OH)2]^{x+}\ X^{n-}_{x/n}\cdot mH_2O$, where M(II) and M(III) and $X^{n-}$ represent any divalent and trivalent cation and the interlayer anion, respectively. These compounds consist of positively charged brucite-like layers, whose net charge is compensated by easily exchanged anions located in the interlayers and have been efficiently used as substrates for

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the electro-deposition of Cd(II) and Pb(II) [16]. In this work, we investigate the possibility to improve the efficiency of the electro-deposition of zinc by mixing LDH together with zinc powder in different ratios.

## 2. Materials and methods

The synthesis procedures of the hydrotalcites $[Zn_4Al(OH)_{10}]_2(CO_3)\cdot nH_2O$, named ZnAl–LDH, was already described in previous publications [17–19]. Different weight ratios LDH:zinc were used, namely, 0:1 (no clay), 1:1, 2:1, and 4:1. In all cases, the weight proportion of additives C65 carbon black (10.5%, Timcal) and polyvinylidene fluoride (5.2%, Solvay) binder solution in N-methyl pyrrolidone (25 mg $ml^{-1}$, Sigma Aldrich) was kept constant. To avoid effects related to mass loading and wet surface, the wet area of the electrode was always maintained around 2 $cm^2$, and the mass loading was controlled in order to obtain electrodes with 2 mg of zinc. A slurry with the corresponding weight proportion of these components was mixed thoroughly for 30 min at 4000 r.p.m. using an ultra-turrax disperser (Ika). The electrodes were prepared by hand-painting on a carbon cloth (Fuel Cell Earth) current collector and were dried at 60 °C prior to use. The efficiency of the zinc electro-deposition was measured by galvanostatic cycling in a Biologic VSP300 potentiostat, using a flooded three-electrode cell containing 15 ml of 0.5 M $ZnSO_4$ aqueous solution, Zn-LDH as working electrode, zinc foil (99.99% Godfellow) as a counter electrode, and Ag/AgCl (3 M KCl) as a reference electrode. Prior to starting the analysis, argon was bubbled for 10 min in solution, and a slow flow was kept during all measurements to avoid the presence of oxygen. The current density applied was based on the amount of zinc present in the electrode and equal to a C/2 rate (where a rate of C/n represents a complete reduction or oxidation of zinc in n hours). Reduction and oxidation steps were limited to 1 h so that at each cycle, theoretically half of the zinc was oxidized and electro-deposited back. X-ray diffraction patterns (XRD) of powder samples and Scanning electron microscopy (SEM) images were recorded using a Siemens D-500 diffractometer with CuKα radiation and a Quanta 3D FEG instrument respectively.

## 3. Results and discussion

### 3.1. Structural characterization of the hydrotalcite sample

The ZnAl–LDH samples were characterized by X-ray diffraction and scanning electron microscopy (Fig. 1a). The XRD patterns are consistent with the characteristic reflections of a hydrotalcite-like material (JCPDS 38–0486) with a rhombohedral symmetry. Impurities of ZnO were also detected, this minor phase is common for hydrotalcites with atomic ratio Zn:Al higher than 2.3 [20]. The diffraction peaks are symmetrical and narrow, indicating a well-crystallized system. This is in accordance with a sheet-like morphology showed in the SEM image (Fig. 1b). The dimension of the particle was in the range of 100 to 400 nm. The structure and morphology obtained are in agreement with previously reported ZnAl–$CO_3$ hydrotalcites [18–19].

### 3.2. Evaluation of the zinc oxidation/reduction process

The electro-deposition of zinc can be described by the following equation (reaction 1):

$$Zn^{2+} + 2e^- \leftrightarrow Zn^0 \qquad E^0 = -0.971V \text{ vs Ag/AgCl (3M KCl)} \qquad (1)$$

Because of the low potential required for reducing zinc, molecular hydrogen could be generated as a side product (reaction 2):

$$2H^+ + 2e^- \rightarrow H_2 \qquad E^0 = -0.210V \text{ vs Ag/AgCl (3 M KCl)} \qquad (2)$$

If this reaction occurs, a fraction of the charge is not used for the Zinc reduction, but is employed in the formation of the $H_2$ bubbles, which

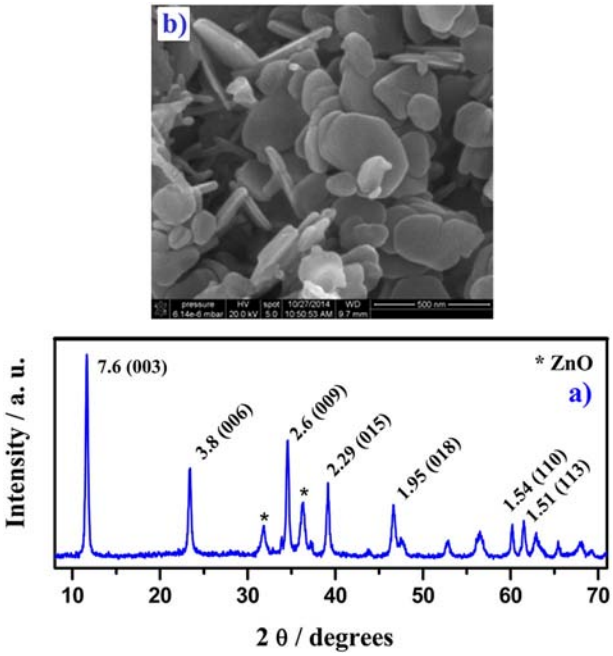


**Fig. 1.** (a) X-ray patterns and (b) SEM images of ZnAl–LDH sample.

can also block part of the surface available for zinc deposition. Hydrogen evolution is also causing a local increase of the pH value, thus favoring the formation of ZnO or $Zn(OH)_2$. These secondary products can passivate the zinc surface and slow down the oxidation of Zn. Recently, Kang et al. [16] reported that the accumulation of different inactive $Zn_4SO_4(OH)_6\cdot xH_2O$ species can also inhibit the reversible deposition/dissolution of zinc. The formation of dendrites on the electrode, accompanied by hydrogen evolution [21], is a common drawback observed in zinc batteries. This process implies a decrease in the efficiency and lifespan of the battery. To evaluate the influence of the LDH on the zinc electro-deposition, the efficiency ($\eta_C$) was defined and calculated as the ratio between the charge flown during the oxidation of metallic zinc and the charge flown during the electro-deposition of $Zn^{2+}$, which in the ideal case should be 100%. In Fig. 2 the efficiency is reported as a function of the number of cycles for the different LDH:Zn ratios, and large deviations from the ideal performance are observed.

For LDH:Zn ratios of 0:1, 1:1, and 2:1, the efficiency was close to 100% in the very first cycles (Fig. 2a). During this early stage, the effect of the side reactions described above were compensated by the excess of zinc that was present on the electrode. Once this zinc was fully dissolved, the efficiency started to decrease and an abrupt drop was observed. The electrode without LDH (ratio 0:1) kept this 100% efficiency for a higher number of cycles. However, at a higher cycle number, the samples with ratio 1:1 and 2:1 reached efficiency values above 92% and close to 95% respectively (Fig. 2b), which were higher than the efficiency reached by the sample without LDH (85%). The sample with ratio 4:1 showed a different profile of the efficiency depending on the number of cycles. Although the starting efficiency was low, probably due to the lower amount of readily available metallic zinc, a continuous increase of the efficiency followed, eventually reaching a value of 98% after 20 cycles. The higher efficiency obtained by the use of LDH as a substrate shows their excellent behavior as a supporting structure for the zinc electro-deposition.

Fig. 3 shows the profile potential vs. time during the Zn electrochemical reduction/oxidation using electrodes with ratio 0:1 and 4:1 at 1st, 50th, and 100th cycles. A potential drop was observed during the first reduction step of the sample LDH:Zn equal to 4:1, as well as in the cycles 50th and 100th cycles for the sample without LDH. We want to stress that there is a clear correlation between the presence of this potential drop and a low efficiency of the electro-deposition process. The value