Electrochimica Acta 109 (2013) 110–116

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

In situ X-ray diffraction investigation of zinc based electrode in Ni–Zn secondary batteries

François Moser[a], Fabrice Fourgeot[b], Robert Rouget[b], Olivier Crosnier[a], Thierry Brousse[a,*]

[a] *Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, CNRS, 2 rue de la Houssinière, BP 32229, 44322 Nantes Cedex 3, France*
[b] *SCPS, 85-91 Boulevard Alsace-Lorraine, F-93115 Rosny-sous-Bois cedex, France*

ARTICLE INFO

Article history:
Received 16 December 2012
Received in revised form 3 July 2013
Accepted 4 July 2013
Available online 15 July 2013

Keywords:
Ni–Zn secondary battery
In situ X-ray diffraction
Bi_2O_3
ZnO

ABSTRACT

In situ/in operando X-ray diffraction coupled with electrochemical cycling of ZnO based electrodes in KOH electrolyte has been used as a powerful tool in order to investigate the influence of additives. The technique has been performed in order to highlight the role of bismuth based conductive additives on the cycling ability of the electrode. It enables to clearly evidence the conversion of zinc oxide to zinc metal. During the first charge, it also helps to visualize the conversion of Bi_2O_3 additive into metallic bismuth prior to ZnO reduction which leads to the formation of an electronic pathway at the nanometer scale complementary from the current collector and the TiN percolation conductive network. Additionally, each Bi_2O_3 grain seems to be converted in a single bismuth grain which is not agglomerated with other bismuth particles even after 50 cycles. This behaviour leads to a steady capacity of the zinc based electrode compared to the same electrode without Bi_2O_3 additive. Subsequently, *in situ* XRD investigation of Zn based negative electrode in nickel–zinc batteries can be a powerful tool to design new composite electrode with long term cycling efficiency.

1. Introduction

Numbers of applications have been envisioned for secondary batteries thanks to research efforts made during the last decade, ranging from portable electronics to electric vehicles. Not only lithium ion batteries are attracting interest for all these uses but there are still a large number of nowadays applications that can accommodate aqueous-based secondary batteries, including hybrid vehicles or uninterrupted power supply. Due to its low cost, low equilibrium potential, good reversibility, high energy density and low environmental impact, zinc has promising perspectives as a material for negative electrode in aqueous-based batteries. However the practical uses of zinc-based electrodes have been limited by poor cycling ability due to dendrite growth, macroscopic change of shape upon repeated charge/discharge cycles and surface passivation. These limitations are consequences of the dissolution of Zn^{2+} species upon oxidation of zinc based electrodes, *i.e.* upon discharging the electrochemical cell when coupled to a nickel hydroxide electrode as it is the case in rechargeable Ni–Zn batteries for example [1]. Ni–Zn rechargeable batteries are assembled with ZnO-based negative electrode and $Ni(OH)_2$ positive one, *i.e.* in the discharge state. Upon charging the cell for the first time, ZnO is reduced to metallic zinc and $Ni(OH)_2$ is oxidized to NiOOH. This causes a first volumetric change of the device since the molar volume of pristine ZnO is larger than that of zinc. On the following discharge, zinc is oxidized to soluble zincate species ($[Zn(OH)_4]^{2-}$) while NiOOH turns back into $Ni(OH)_2$. On subsequent charge, zincates are reduced back to zinc, but, at the macroscopic scale of the negative electrode, this reduction can only occur where electronic transfer is possible, *i.e.* at the interface between an electronically conducting grain connected to the current collector through a conductive pathway, and the electrolyte containing the soluble zincates species. Additionally, solid oxidized zinc species *e.g.* remaining ZnO or precipitated $Zn(OH)_2$, in contact with the electronically conductive grain can also be reduced to metallic zinc. Thus, charge/discharge cycles induce the breathing of the negative electrode which is repeatedly submitted to volume expansion/contraction. Furthermore, the formation of metallic zinc upon charging occurs preferentially where current density is the most important, *i.e.* close to the edges of the current collector. This induces the formation of zinc aggregates on the edges of the current collector, leading to a change in the shape of the electrode. Indeed, before the first charge, ZnO is homogeneously distributed throughout the electrode due to standard and well managed fabrication process, while after few charge/discharge cycles, zinc species are concentrated close to the edges of the current collector. In addition, deposition of zinc does not occur as a flat layer on the current collector but rather as dendrites that can further grow and create

* Corresponding author. Tel.: +33 2 40 68 31.
E-mail address: 73Thierry.brousse@univ-nantes.fr (T. Brousse).

0013-4686/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.electacta.2013.07.023

short circuits with the positive electrode after few charge/discharge cycles. Dendrites growth and change of shape are the main drawbacks that limit the cycling ability of zinc based electrodes in Ni–Zn batteries.

Different solutions have been proposed to limit or cancel these drawbacks. Calcium hydroxide additives for example [2–7] can limit the solubility on zincate species thus preventing their diffusion in the liquid electrolyte and limiting the aggregation of zinc upon charging the cell. Hydrogel electrolyte [8–11] can also prevent the solubility of zincates and limit dendrite growth due to the high viscosity of the electrolyte. However, such additives cannot be efficient if the current density is not homogeneously distributed throughout the electrode. This suggests that the distribution of the current at the scale of the current collector (≈100 μm in the case of metallic grid or metallic foam for example) is not satisfactory and must be downsized to μm or even nm range. This can be done by adding stable conductive additives such as transition metal nitrides, TiN being one of the most promising compounds. Most beneficial effects of metal nitride additives include: suppression of H_2 formation, increased electronic conductivity of the ZnO electrode and better charge dispersion as a secondary electronically conductive pathway. Titanium nitride has also been used for stabilizing zinc re-deposition. TiN is often added as a 1–10 μm powder [12]. The effect is remarkable since it helps to stabilize the shape of the negative electrode for several hundred of cycles. An even smaller scale of current distribution can be achieved *via* the use of nanoscale conductive additives. Since metallic materials are difficult to synthesize on an industrial scale as nanometric powders, oxides are most preferentially used. Nanoscaled Bi_2O_3 additives for example [1,13,16,17], lead to improved cyclability of zinc-based electrodes. Performances of zinc-based electrodes are related to nature, concentration and dispersion of such additives. However, their effect and their influence on the structural changes of the zinc based electrode are only poorly documented in the literature. Even Linden's Handbook on batteries [18] mentioned that there have been a large variety of chemicals added to the zinc negative electrode to improve cycle life and aid electrode manufacturing, but their role is not detailed. More specifically, the role of these nanometric oxides is not well understood. In fact, upon charging the cell for the first time, the reduction of Bi_2O_3 to metallic bismuth occurs at a quite lower potential than the reduction of ZnO to metallic zinc according to Pourbaix diagram [19]. Thus, the first charge creates a nanometric network of metallic bismuth particles connected to TiN conductive additive and further to the metallic current collector. Upon subsequent discharge, the potential of the negative electrode does not reach the potential of bismuth oxidation (−0.45 V *vs* ENH at pH = 14), while zinc is further oxidized to zincate species (−1.21 V at pH = 14). With the preservation of such hierarchical conductive network (current collector, TiN micrometric size particles and metallic bismuth nanometric size particles) upon repeated charge/discharge cycles, the distribution of current density is quite homogeneous throughout the zinc-based electrode, thus preventing shape change and improving the cycle life up to thousand of cycles. It can be noted that the fine tuning of the electronic conductivity in zinc based batteries not only plays a role in improving the electrode kinetic, as what is done in Li-ion battery electrodes for example when carbon coating is used, but it is also the keypoint for maintaining the cycling ability of the electrode since it must monitor zinc electrocrystallization after the first formation cycle. Surprisingly, unlike the general trend observed for lithium ion battery electrodes [20–22], no *in situ* XRD measurements have been performed in addition to *ex situ* characterization to expand knowledge for understanding reaction mechanism linked to the use of Bi_2O_3 additives and subsequently for improving electrochemical properties of zinc-based electrodes. Even recent studies aiming at improving the cycling ability of zinc based electrodes by Bi_2O_3 doping [14–16] do not provide evidences of the role of bismuth upon charging/discharging the cell from a structural and microstructural point of view. The studies are mainly focussed to the electrochemical improvement of the electrode rather than on the comprehension of which changes occur in the composite electrode.

In order to highlight the role of nanoscaled bismuth oxide additive in ZnO electrodes for Ni–Zn rechargeable battery we have investigated the structural changes occurring upon cycling. Thus, the present work focuses on the development of an *in situ/in operando* X-ray diffraction measurement set-up that can improve the comprehension of structural and microstructural behaviour of additives during zinc-based electrode cycling. This set-up is also dedicated to the study of cycling ability of the electrode, thus drastic conditions for limiting the cycling ability have been intentionally chosen. With such conditions, standard zinc-based electrode will only sustain few tens of cycles and not hundreds as in a real life device.

2. Experimental

Zinc-based electrodes were prepared by incorporating slurries containing ZnO (average diameter size 250 ± 50 nm), TiN (average diameter size 1 ± 0.5 μm) and Bi_2O_3 powders (average diameter size 100 ± 20 nm, Alfa Aesar, 99% purity) with polytétrafluoroéthylène (PTFE) in a copper foam substrate that is subsequently laminated. The electrode which will serve as blank sample, Zn-wB (wB standing for "without bismuth oxide") contains only ZnO, TiN and PTFE, while Bi_2O_3 was added to the composition of the optimized electrode, Zn-B (Table 1). ZnO-based electrodes have been designed to be the limitative electrodes, with 658 mAh g^{-1} of ZnO maximum theoretical capacity, which translates into ≈130 ± 10 mAh for the electrode design (20 mm × 20 mm × 0.6 mm) chosen in this study. The $Ni(OH)_2$ positive electrodes (310 mAh for 28 mm × 28 mm × 0.9 mm) have more than twice the capacity of the zinc-based one. The capacities of the electrodes are designed to accelerate the zinc electrode ageing. Two different compositions of Zn-based electrodes have been used, namely with and without nanoscaled Bi_2O_3 powders, named respectively Zn-wB and Zn-B.

A special electrochemical cell has been designed to perform *in situ* XRD experiments (Fig. 1a). The positive electrode consists of a thick $Ni(OH)_2$ electrode parallel to the ZnO based working electrode, and is located on the bottom of the device, supported by a mineral foam which acts as an electrolyte reservoir. Both electrodes are separated by a conventional PP-PA separator soaked with the electrolyte and placed into a Teflon cavity of 80 mm × 60 mm × 10 mm. The zinc-based negative electrode is located at the top position for X-rays exposure. *In situ* XRD cell is filled with 7 M KOH electrolyte with special care to let the top surface of working electrode not covered with the electrolyte, thus preventing huge X-ray attenuation.

The details of the *in situ* cell are given in Fig. 1b. In order to maintain the top surface of zinc-based electrode into the focal plane of the X-ray beam, two Teflon bars were used. Teflon bars have also been useful to influence the volume expansion of electrodes towards the bottom of the system thanks to the use of mineral foam which can contract and expand reversibly, also used as a reservoir for electrolyte (Fig. 1b).

X-ray powder diffraction (XRD) patterns were recorded using a PANanalytical X'Pert Pro diffractometer operated in Bragg-Brentano reflection geometry with a Long Line Focus Cu anode X-ray source, and a X'Celerator RTMS detector between 20° and 80° angle range. Measurements were performed with a Multi Purpose Sample Stage (MPSS) enabling to adjust the surface of