Bulgarian Chemical Communications, Volume 48, Number 1 (pp. 61– 65) 2016

Novel current collector and active mass carrier of the zinc electrode for alkaline nickel-zinc batteries

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Received January 13, 2015, Revised July 30, 2015

A new current collector and electrode mass carrier based on copper foam is developed and applied in constructing pasted zinc electrode for alkaline nickel-zinc batteries. It is suggested that the microcellular structure of the foam matrix assures uniform volume conductivity of the zinc electrode mass, facilitates the electron transport between the electrochemically active electrode material and the current collector, improves the mechanical stability of the electrode, also helping to minimize dendrite formation during charging. It is shown that the surface modification of the electrode foam matrix by duplex tin/zinc coating leads to considerable reduction of gas evolution on the current collector during the charging process. The investigation on the performance of nickel-zinc battery cells has definitely proved the possibility of application of the newly developed current collector and active mass carrier for pasted zinc electrodes in nickel-zinc batteries.

Keywords: current collector, electrode mass carrier, copper foam, zinc electrode, nickel-zinc batteries

INTRODUCTION

The interest to rechargeable alkaline nickel-zinc batteries is largely stimulated by the advantages offered by this electrochemical system – high specific energy density (55 – 85 Wh kg^{-1}), high power density (140 -200 W kg^{-1}), high voltage (1,73 V), abundant low-cost materials and environmentally acceptable chemistry. There is no use of heavy metals (Hg, Pb, Cd), no flammable active materials and electrolytes and a simple recycling process of the metal recovering. Besides, the electrochemical system Ni-Zn is similar to the widely used in the practice Ni-Cd system and battery technology but is advantageously environmentally friendly by replacing the toxic cadmium with common zinc [1-5].

Since the zinc electrode also demonstrates fast electrochemical kinetics, the battery is ideally suited to high discharge rate applications such as power tools, household appliances, toys, electric bikes and hybrid electric vehicles. Nickel-zinc batteries are the ideal choice when there is a need for a small, lightweight power source at a cost significantly lower than lithium-ion battery [1,5,6].

The battery life is largely determined by the life of the zinc anode – usually a paste type electrode with an electrochemically active composite electrode mass based on powder ZnO and additives for improving electrochemical performance (e.g. calcium hydroxide, bismuth oxide, indium oxide, carbon additives, conductive ceramic materials, etc.) of the anode. However, the zinc electrode suffers from a short cycle life due to degradation of the zinc anode material because of dendrite growth during the charging process (penetrating the cell separator and causing internal short circuits), high solubility of the ZnO (a discharge product of the zinc anode) and the metal zinc in highly alkaline battery electrolytes. The electronic conductivity of ZnO is also rather poor and this is the main reason for the electrochemical heterogeneity of the anode mass. Besides, the zinc electrode loses active surface area during charge/discharge cycling, which results in gradual changes in the electrode shape and loss of capacity [1,3,7,8].

As current collectors and electrode mass carriers of the zinc electrode usually copper or copper alloys in the form of grid, foil, perforated plate or rugged strip are used. Serious disadvantage of those carriers is the possibility of intensive gas evolution on the electrode during charging due to the low overpotential of hydrogen evolution on those metals which results in decreasing the effectiveness of the charging cycle and especially – of the mechanical stability of the electrode mass, thus reducing the life of the zinc electrode.

The aim of the present paper is to develop a new current collector and active mass carrier for the zinc electrode of nickel-zinc alkaline rechargeable battery using modified copper foam.

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EXPERIMENTAL

Design of a current collector and active mass carrier of the zinc electrode based on copper foam matrix

The current collector and electrode mass carrier of the zinc electrodes for prismatic type nickel-zinc batteries is a rectangular matrix of copper foam covered with electrodeposited tin (base) and zinc layers. The microcellular structure of the foam assures uniform volume conductivity of the zinc electrode mass, facilitates the electron transport between the electrochemically active mass and the current collector and improves the mechanical stability of the electrode as a whole. It also helps to minimize formation of dendrites during charging process. The zinc coating and especially – the tin coating isolate the copper substrate from the battery electrolyte and assure minimal gas evolution on the electrode during charging because of the high hydrogen overpotential on those two metals. Besides, the zinc layer is an additional source of metallic zinc for the current generation reaction which would have a beneficial effect on the magnitude and stability of the electrode capacity during charge/discharge cycling of the battery.

The electrode matrix is cut from copper foam in rectangular form with appropriate dimensions, enforced along one of the longer edges by welding a copper strip bar with a tail for electric contact, and then subjected to electrochemical deposition, first of tin coating (5-10 μm thick) and after that of zinc coating (10-20 μm thick) [9].

Electroplating of tin and zinc layers on the copper foam matrix

The electrode matrix is first subjected to a conventional surface treatment: degreasing in ethanol solution, washing, pickling in dilute solution of hydrochloric acid and washing. The electroplating of the tin layer is performed from an electrolyte containing H_2SO_4, $SnSO_4$ and wetting additive ZC-1. The zinc layer is deposited from an electrolyte containing $ZnSO_4.7H_2O$, NH_4Cl, H_3BO_3, wetting additive ZC-1 and brightener ZC-2. The electroplating is realized using a shaking bar for continuous reflexive movement of the sample with an aim for a better penetration of the electrolyte into the foam volume. The surface morphology of the copper foam electrode matrices without and with tin and zinc coatings is studied using scanning electron microscope JEOL JSM-6390 for SEM analysis.

Electrochemical properties of the new current collector

The main objects of study are the corrosion behavior of the modified electrode matrix and the hydrogen evolution on that matrix applying electrochemical polarization techniques. The investigation is performed in an alkaline electrolyte normally used in nickel-zinc batteries [9] with composition: KOH (400 g/l), NaOH (35 g/l), $LiOH.H_2O$ (18 g/l), $KF.2H_2O$ (30 g/l), $Na_3PO_4.12H_2O$ (50 g/l). As model electrode matrix samples of copper plate (dimensions 2.0 × 1.0 cm) with different coatings are used. The potentiodynamic curves of the samples are obtained by linear polarization method (scanning rate of 1 mV/s) using VerStat 4 PAR apparatus and a conventional three-electrode electrochemical cell with platinum plate as a counter electrode and saturated calomel electrode as a reference electrode. All measurements are carried out at room temperature.

Preparation and testing of the pasted zinc electrode in an experimental nickel-zinc cell

A matrix of copper foam (Circuit Foil Luxembourg Sarl, Luxembourg) with dimensions 5.0 × 3.0 cm and thickness 0.15 cm is used for current collector and active mass carrier of the zinc electrode. The electrodeposited tin and zinc layers on the foam matrix have thickness of 5 and 10 μm, respectively. The active electrode mass in the form of paste with composition: ZnO – 85,0%, $Ca(OH)_2$ – 4,0 %, Bi_2O_3 – 4,0%, Acetylene black – 2,0%, polytetrafluoroethylene – 4,0 % and carboxymethylcellulose – 1,0 % is uniformly incorporated into the cellular structure of the matrix. The pasted electrode is dried at 70 ^{0}C for 2 h, pressed at 30 MPa and then mounted into double separator pockets made of separators Celgard C3501 and PGA-Text. The electrode-separator assembly is soaked with battery electrolyte under vacuum for 10 min before mounting in the battery cell. The composition of the electrolyte is: KOH - 400 g/l, NaOH - 35 g/l, $LiOH.H_2O$ - 18 g/l, $KF.2H_2O$ - 30 g/l, $Na_3PO_4.12H_2O$ - 50 g/l, the balance - H_2O, and is saturated with ZnO (approx. 20 g/l) [9].

Sintered type of nickel electrodes (CLAIO, Poznan, Poland) with dimensions 5.0 × 3.0 cm and thickness 0.12 cm are used for cathodes in the experimental nickel-zinc battery cell. The electrodes are wetted directly with the electrolyte before mounting in the cell using the same evacuation procedure.

The experimental nickel-zinc prismatic battery cell is assembled with two nickel cathodes and one zinc anode, prepared as described above. The cell is subjected to electrochemical charge/discharge test using a multichannel automated battery testing apparatus type CDT10. The apparatus gives a possibility for a complex control and monitoring of the main cell parameters during charge/discharge cycling - cell voltage and current, reference potential, capacity and temperature.

RESULTS AND DISCUSSION

The cellular structure of the copper foam electrode matrix in “as received” conditions (without coating), with tin coating only and with duplex tin-zinc coating is illustrated by SEM images on Fig.1. As seen, the cellular structure of the foam matrix practically does not change after plating of the tin coating and the duplex tin-zinc coating, and both coatings are uniform. This microcellular structure of the electrode matrix, as already noted, not only facilitates the electron transport between the electrochemically active electrode mass (based on ZnO – a material characterized with low electron conductivity) and the current collector, but it also improves the mechanical stability of the electrode as a whole.

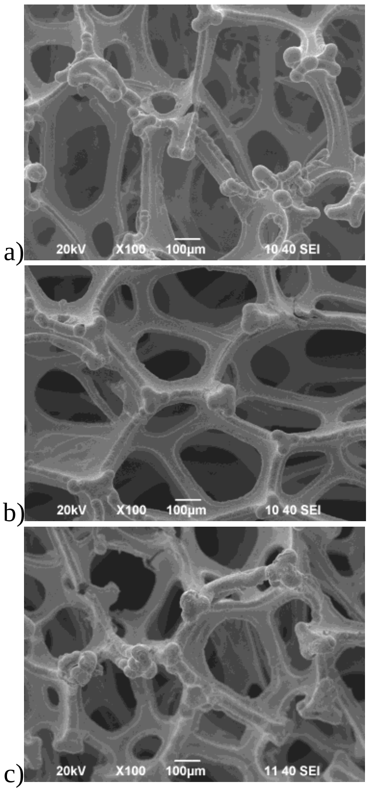

Fig. 1. SEM images of copper foam in “as received” condition (a), with tin coating (b) and with tin and zinc coatings (c).

The main electrochemical properties of the modified copper foam electrode matrix are demonstrated by the polarization curves of the model samples of copper plate with different coatings (tin and duplex tin-zinc) obtained in the nickel-zinc alkaline battery electrolyte, as shown in Fig. 2. The working zone of the zinc electrode in the nickel-zinc battery – from the maximal potential of charging (-1.7 V, SCE) to the minimal potential of discharging of the electrode (-1.4 V, SCE) is also shown on the same figure.

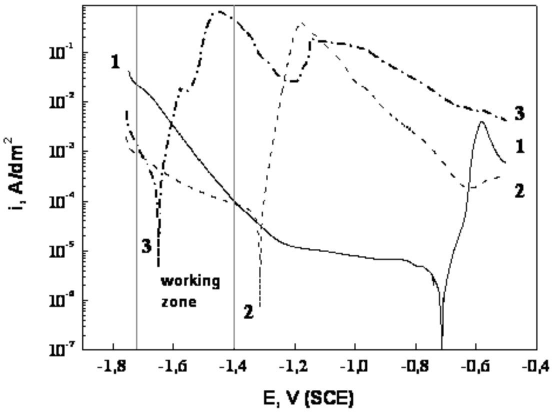

Fig. 2. Potentiodynamic polarization curves of copper plate (1), copper plate with tin coating (2) and with tin and zinc coatings (3) in the battery electrolyte.

The following conclusions can be made from the results of the polarization studies: (a) the presence of tin coating, and especially – of zinc coating on the copper surface significantly shifts the corrosion potential of the system in negative direction; (b) as expected, copper shows high corrosion stability in the highly alkaline battery electrolyte; (c) the rate of hydrogen evolution on the copper surface in the working zone of the zinc electrode is much higher (1-2 orders of magnitude) in comparison to the rate of hydrogen evolution on zinc coating and especially – on tin coating, and this difference is better expressed at more negative potentials (higher potentials of charging of the zinc electrode); (d) the anodic dissolution of zinc (cf. curve 3) is active in the whole working zone which suggests that the deposited zinc layer would not only reduce the hydrogen evolution on the matrix but it could also serve as an additional source of active zinc for anodic reaction on the zinc electrode, especially at prolonged exploitation of the battery. The surface modification of the copper foam electrode matrix by tin and zinc coatings would strongly restrict the gas evolution on the matrix; (e) there is practically no anodic dissolution of tin in the whole working zone which means that the tin coating is cathodically protected by the zinc layer and it would reliably isolate the copper matrix from the battery electrolyte and strongly restrict the gas evolution in case of partial uncovering of the copper surface of the matrix. Thus, the above results definitely proved the choice of duplex tin-zinc coating on the copper foam current collector.

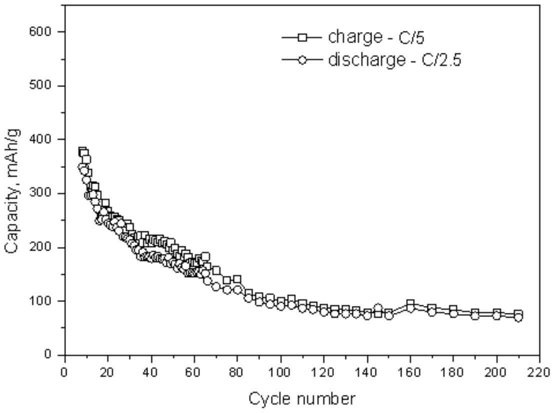

Fig. 3. Dependence of the charge and discharge capacity on the number of cycles of the experimental nickel-zinc battery cell at current load procedure C/5 – C/2.5 (C=1.0 Ah is the nominal capacity of the cell).

The electrochemical testing of the zinc electrode constructed with modified copper foam matrix as current collector and active mass carrier in the experimental nickel-zinc cell is carried out at constant current mode from full charged state of the electrode to full discharge at room temperature. First, a forming cycle at charge/discharge procedure C/20 – C/10 and 5 cycles at normalizing procedure C/10 – C/5 (where C=1.0 Ah is the nominal capacity of the cell) are performed and then the cell is subjected to continuous cycling charge/discharge at procedure C/5 (0.2 A) – C/2.5 (0,4 A) up to 250 cycles. In Fig. 3 the dependence of the charge and discharge capacity on the number of charge/discharge cycles is shown. The data in the figure illustrate well the very good characteristics of the zinc electrode – high specific discharge capacity (above 100 mAh/g) at high current load (0.4 A), high charge/discharge efficiency (above 95 %), good cycleability and stability of the capacity, especially at prolonged cycling.

CONCLUSION

New current collector and electrode mass carrier based on copper foam is developed and applied in constructing pasted zinc electrode for alkaline nickel-zinc batteries. It is suggested that the microcellular structure of the foam assures uniform volume conductivity of the active mass, facilitates the electron transport between the electrochemically active electrode material and the current collector, improves the mechanical integrity of the electrode, and helps to minimize formation of dendrites during charging process.

It is established that the modification of the copper surface with duplex tin/zinc coating results in a considerable reduction of the rate of the hydrogen evolution at charging conditions of the zinc electrode, thus restricting the gas evolution on the electrode foam matrix during charging cycle. In addition, the zinc layer is an additional source of metallic zinc for the current generation reaction which would have a beneficial effect on the magnitude and stability of the electrode capacity, especially at prolonged cycling of the battery.

The electrochemical testing of pasted zinc electrodes constructed with modified copper foam matrix as current collector and active mass carrier in an experimental alkaline nickel-zinc battery cell has demonstrated an excellent performance of the electrode – good cycleability, high and stable specific discharge capacity, high charge/discharge efficiency, etc. Thus, all the results proved definitely the possibility of application of the newly developed current collector and active mass carrier for pasted zinc electrodes in alkaline nickel-zinc batteries.

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НОВ ТОКОВ КОЛЕКТОР И НОСИТЕЛ НА АКТИВНАТА МАСА НА ЦИНКОВ ЕЛЕКТРОД ЗА АЛКАЛНИ НИКЕЛ-ЦИНКОВИ БАТЕРИИ

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Постъпила на 13 януари 2015 г.; коригирана на 30 юни 2015 г.

(Резюме)

Нов токов колектор и носител на електродната маса, основан на медна пяна, е разработен и приложен за конструиране на пастов тип цинкови електроди за алкални никел-цинкови батерии. Микроклетъчната структура на електродната матрица от медна пяна осигурява равномерна обемна проводимост на цинковата електродна маса, улеснява преноса на електрони между активния електроден материал и токовия колектор, подобрява механичната устойчивост на електрода и ограничава образуването на дендрити при зареждане на електрода. Показано е, че повърхностната модификация на електродната матрица с двуслойно калай/цинково покритие води до значително намаляване на отделянето на газ върху токовия колектор в процеса на зареждане на електрода. Изследванията върху работата на никел-цинкови батерии доказват убедително възможността за прилагане на разработения токов колектор и носител на активната маса на цинкови електроди за никел-цинкови батерии.