



Superconducting BSCCO Ceramics as Additive to the Zinc Electrode Mass in the Rechargeable Nickel-Zinc Batteries

L. Stoyanov¹, S. Terzieva², A. Stoyanova^{3*}, A. Stoyanova-Ivanova⁴, M. Mladenov⁵, D. Kovacheva⁶, R. Raicheff⁷

^{1,3*,5,7}Institute of Electrochemistry and Energy Systems – BAS, 10 G. Bonchev Str., 1113 Sofia, Bulgaria.

²Institute of Solid State Physics – BAS, 72 Tzarigradsko Chaussee, Blvd., 1784 Sofia, Bulgaria.

⁴Institute of Solid State Physics – BAS, 72 Tzarigradsko Chaussee, Blvd., 1784 Sofia, Bulgaria.

⁶Institute of General and Inorganic Chemistry – BAS, 10 G. Bonchev Str., 1113 Sofia, Bulgaria.

Abstract

The electronic conductivity of the main component of the zinc electrode in the rechargeable zinc-nickel battery – ZnO, is rather poor and this is the main reason for the electrochemical heterogeneity of the anode mass and the loss of active surface area during charge/discharge cycling with a corresponding negative effect on the electrode characteristics. In the present work, the possibility of application of superconductive cuprate Bi-Pb-Sr-Ca-Cu-O (BSCCO) ceramic as a multifunctional conductive additive to the zinc electrode mass is studied. Powder samples of the BSCCO ceramic $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ are produced by two-stage solid-state synthesis and they are physicochemically characterized. The XRD patterns and SEM observation reveal a well crystallized single phase of superconducting 2212 BSCCO system with average crystallite size 5-10 μm . The chemical stability of BSCCO ceramics in highly alkaline medium of the Ni-Zn battery is confirmed by structural and morphological analysis (XRD, SEM and EDX) of the samples before and after prolong exposure (96 h) to 7M KOH. The electrochemical tests are carried out by a specially designed prismatic alkaline Ni-Zn battery cell with conventional sintered type nickel electrodes and pasted zinc electrode with active electrode mass based on ZnO (88 wt.%) and addition of BSCCO powder or acetylene black as conductive additives. The study shows that the zinc electrode with BSCCO superconducting ceramic additive exhibits very good cycleability, remarkable capacity stability and much higher discharge capacity at prolong charge/discharge cycling in comparison to the zinc electrode with the "classic" carbon conductive additive. It is suggested that the addition of BSCCO ceramics improves not only conductivity of the electrode mass and reduces the gas evolution but also stabilizes porosity structure. The results obtained prove the possibility of application of superconducting BSCCO ceramics as a multifunctional additive to the active mass of the zinc electrodes for alkaline battery systems.

Keywords: Superconducting Ceramics; Zinc Electrode; Electrode Mass; Additives; Alkaline Nickel-Zinc Battery.

1. Introduction

The rechargeable alkaline Ni-Zn battery is an economically visible and ecologically friendly alternative of the widely used in the practice alkaline Ni-Cd battery. Besides, Ni-Zn battery offers a number of advantages as high both specific energy density (up to 85 Wh kg^{-1}) and power density (up to 200 W kg^{-1}), high voltage (1,73 V), good low-temperature performance, abundant low-cost materials, environmental friendly chemistry, no use of flammable active materials and electrolytes as well as a simple recycling process of metal recovering. Since the zinc electrode demonstrates fast electrochemical kinetics, the battery is ideally suited as energy storage devices for high discharge rate applications such as power tools, household appliances, toys, electric bikes and hybrid electric vehicles [1-6].

The battery life is largely determined by the zinc electrode, and especially – by the life of the anode mass. The zinc electrode is a paste type with a composite anode mass, with main component - electrochemically active ZnO powder (80-95 %) and various additives (e.g. $\text{Ca}(\text{OH})_2$, Bi_2O_3 , PbO , SnO_2 , TiO_2 , organic binders, dispersants, etc.) for improving electrochemical characteristics of the electrode [1, 2, 6-12].

The electronic conductivity of the major active electrode material – ZnO, however is rather poor and this is the main reason for the electrochemical heterogeneity of the anode mass and the loss of active surface area during charge/discharge cycling with a corresponding negative effect on the zinc electrode characteristics [1,13,14]. In order to improve the conductivity of the zinc electrode mass carbon powder materials (e.g. graphite, acetylene black, etc.) are usually applied as conductive additives but this may results in an increase of the hydrogen gas evolution during charging with related decrease of charge/discharge effectiveness as well as the possible mechanical destruction of the electrode mass [15].

Recently, in course of improvement the zinc electrode performance, a considerable attention is attracted on application of different conductive oxides and ceramics as additives to the anode masses based on zinc oxide [16-18]. Thus, it is shown that the addition of titanium sub-oxides conductive ceramics to the electrode mass leads to a higher discharge capacity and superior cycle stability in comparison with the zinc electrodes with acetylene black additive or without conductive additives, which is attributed to high both conductivity and corrosion resistance as well as high overpotential of hydrogen evolution on conductive ceramics [16]. Conductive powder ceramic with nominal composition of $(\text{ZnO})_{0,92}(\text{Bi}_2\text{O}_3)_{0,054}(\text{Co}_2\text{O}_3)_{0,025}(\text{Nb}_2\text{O}_5)_{0,00075}(\text{Y}_2\text{O}_3)_{0,00025}$ is investigated as additive to the zinc electrode and it is found that the ZnO/conductive ceramic nanocomposite demonstrates improved electrochemical properties, such as higher discharge capacity, cycling stability and efficiency compared to the zinc electrode with pure nanosized ZnO. The positive effect of the addition of conductive ceramic is explained with formation of a highly conductive network of metals Bi, Co and Y during cycling, which helps to improve the electrical contact between ZnO particles and increases the actual reaction surface area [17, 18].

In this respect, it is interesting to investigate also the possibilities for application of high temperature superconductive (HTS) ceramics as additive to the zinc electrode mass for Ni-Zn batteries, thus contributing to a longer battery life by improving the conductivity and structural stability of the anode. The superconductors of the cuprate systems Y-Ba-Cu-O (YBCO ceramics) and Bi-Sr-Ca-Cu-O (BSCCO ceramics) are at present the most advanced high temperature superconductive materials with potential large-scale engineering application [19-21].

The chemical stability and the interaction of the high-temperature oxide superconductors with the environment seems to be one of the most important factors for their practical application. Despite the large number of papers on physical properties, those related to the interaction of the HTS materials with the environment are surprisingly few, as those dedicated to the chemical stability of HTS in water [22-25]. It is suggested that the hydrolysis may reduce the volume of the superconductive phases while the resistivity remains practically unchanged. The interaction of BSCCO HTS $\text{Bi}_{1,4}\text{Pb}_{0,6}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ samples with water and aqueous solutions of NaCl and NaOH (after long-term exposure to the solutions) is shown to cause decrease of the relative volume of superconducting phases from 17% to 57% [25].

In a previous papers [26] the possibility of using YBCO ($\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$) powder superconducting ceramics as an additive to the zinc electrode mass of nickel-zinc alkaline rechargeable batteries is studied intensively. First, the high chemical resistance of the ceramic to the battery electrolyte has been confirmed by structural and surface morphology observations as well as magnetic measurements of ceramic samples after prolong exposure to the alkaline electrolyte. The electrochemical tests have shown that the zinc electrode with YBCO ceramic additive (7 wt.%) exhibits good cycling operation ability and capacity stability, and higher (by about 30%) specific discharge capacity than the zinc electrode with a “classic” conductive carbon additive.

The aim of the present paper is to investigate the possibility of application of superconductive cuprate BSCCO ($\text{Bi}_{1,7}\text{Pb}_{0,3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$) ceramics as a multifunctional conductive additive to the zinc electrode mass in rechargeable alkaline Ni-Zn batteries.

2. Experimental

2.1. Synthesis of BSCCO Ceramics and ZnO

Powder samples of $\text{Bi}_{1,7}\text{Pb}_{0,3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ are produces by two-stage conventional solid-state synthesis from high-purity (99,99 %) oxides - Bi_2O_3 , PbO , CuO and SrCO_3 and CaCO_3 after thorough mixing and grinding. First stage is a heat treatment at 780 °C for 24 hours in air. After this first synthesis, the powder obtained is grinded and pressed in pallets (5-6 MPa), and sintered at 830°C for 48 hours in air atmosphere.

The electrochemically active nanosized powdered ZnO is produced by a solution combustion method using as initial compound $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and sucrose. The amorphous powder oxide material produced after evaporation of the water is subjected to thermal treatment at 600 °C in order to obtain the appropriate size of the crystallites.

2.2. Physicochemical Characterization of Electrode Materials

The X-ray diffraction patterns of BSCCO ceramic, ZnO and zinc electrode mass powder samples are collected within the range from 5.3 to $80^\circ 2\theta$ with a constant step $0.02^\circ 2\theta$ on a Bruker D8 Advance diffractometer with Cu K α radiation and a LynxEye detector. The phase identification is performed with the Diffracplus EVA v.15 program using the ICDD-PDF2 (2009) Database. The mean crystallite size is determined with Topas-4.2 software package using the fundamental parameters peak shape description including appropriate corrections for the instrumental broadening and diffractometer geometry [27].

The microstructure of the samples is studied by means of a Zeiss EVO MA-15 scanning electron microscope (SEM) with LaB6 cathode on the polished cross-section of the samples. The chemical composition is determined by X-ray microanalysis using energy dispersive spectroscopy (EDS) on an Oxford Instruments INCA Energy system. The qualitative and quantitative analyses are carried out at an accelerating voltage of 20 kV.

The electric resistance of the electrode mass with different conductive additives of the zinc electrodes is also measured using a high-frequency measuring system.

2.3. Chemical stability of BSCCO Ceramics in Alkaline Medium

The chemical stability of the superconducting BSCCO ceramic $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ in highly alkaline medium is studied by analyzing samples of the ceramic before and after prolonged exposure to 7M KOH solution, normally used as a basic electrolyte in N-Zn alkaline batteries. The pellets of the sintered ceramic samples (10 mm diameter, 2 mm thick) are first soaked in 50 ml of the test solution and then exposed to the same solution for 96 hours. After the exposure, the samples are removed from the solution, dried at room temperature and subjected to structural and morphological analysis using XRD, SEM and EDX methods. The superconducting critical temperature of the BSCCO ceramic before and after the treatment in the alkaline solution is also obtained from resistivity measurements of the samples by the four probe contact method [28].

2.4. Preparation of Pasted Zinc Electrodes and Assembling of Ni-Zn Battery Cells

The paste-type zinc electrodes used in the present study are prepared by coat and press method [6,30]. The electrode mass is composed by powder ZnO (88 wt.%), a conducting additive – superconducting ceramic powder BSCCO (7 wt.%) and binding agents – polytetrafluorethylene (PTFE, 4 wt.%) and carboxymethylcellulose (CMC, 1 wt.%) [30]. The electrode mass is thoroughly mixed with certain amount of distilled water to form mushy paste. A matrix of copper foam (Circuit Foil Luxembourg Sarl, Luxembourg) with dimensions 5,0 x 3,0 cm and thickness 0,15 cm is used for current collector and active mass carrier of the zinc electrode. The paste (about 3,0 g) is uniformly spread and incorporated into the cellular structure of the matrix. The pasted electrode obtained is dried at 70°C for 2 h, pressed to a thickness of 0.11 cm at 30 MPa and then mounted into a separator pocket made of a polypropylene type microporous separator (Celgard C3501, Celgard, USA). A solution of 7M KOH saturated with ZnO is used as a battery electrolyte. The electrode-separator package is soaked under vacuum with battery electrolyte for 10 min before mounting in the prismatic nickel-zinc battery cell. For comparison, similar zinc electrodes with electrode mass composed by ZnO (88 wt.%), Bi_2O_3 (wt.4,0%), PbO (wt.1,0%) and the same binding agents – polytetrafluorethylene (4 wt.%) and carboxymethylcellulose (1 wt.%), but containing a conventional conductive carbon additive – acetylene black (2,0 wt.%) are also fabricated, applying the same technological procedure [30].

Sintered type of nickel electrodes (CLAIO, Poznan, Poland) with dimensions 5,0 x 3,0 cm and thickness 0,12 cm, and a nominal capacity about two times higher than that of the zinc electrodes, are used for cathodes in the nickel-zinc battery cell. The electrodes are directly wetted with the electrolyte before mounting in the cell using the same evacuation procedure. The container of the prismatic battery cell is made of a transparent plastics material and the cell is assembled with two nickel cathodes and one zinc anode.

2.5. Electrochemical Testing of Ni-Zn Battery Cells

The experimental nickel-zinc battery cells are subjected to electrochemical charge/discharge tests using a multichannel automated battery testing apparatus type CDT10 (PMC Ltd., Sliven, Bulgaria). 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. The electrochemical test of the zinc electrode developed is carried out at constant current mode from full charged state of the electrode to full discharge at room temperature and procedure worked out at IEEES-BAS. First, a slow forming cycle at charge/discharge procedure C/20 – C/10 and 3 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 cycling procedure at different increasing discharged current load (10 cycles at every current load) - from C/2.5 (0.4 A) to 9C (9.0 A). Then, after 3 cycles at normalizing procedure C/10 – C/5, the cell is subjected to a continuous cycling (up to 500 cycles) at charge-discharge procedure C/5 – C/5 (0.2 A). The zinc electrodes are characterized by the charge-discharge cycling behavior, discharge capacity at different current load, capacity retention and cycling life.

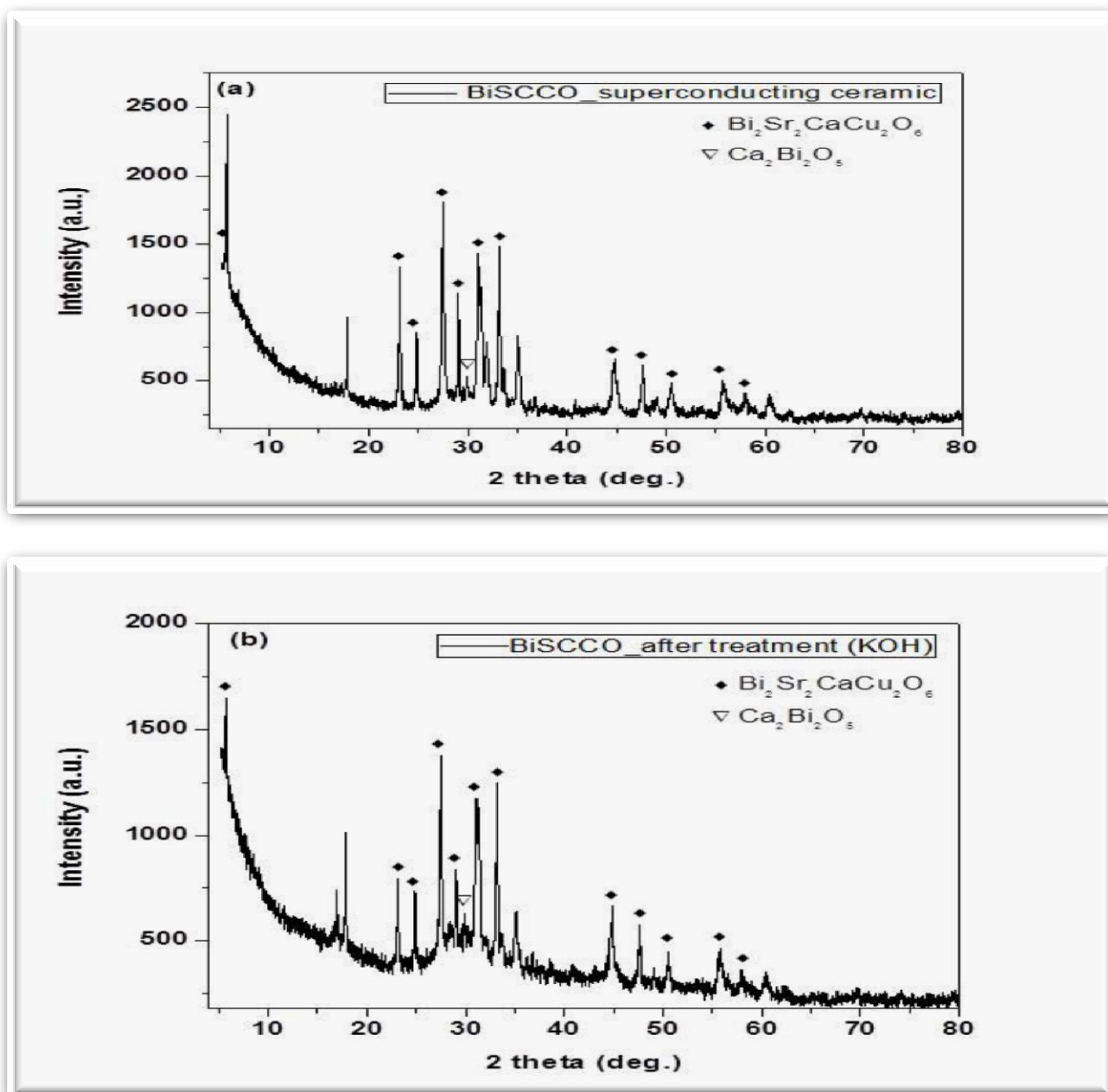
3. Results and Discussion

3.1. Chemical Stability of BSCCO Ceramics in Alkaline Medium

The X-ray diffraction patterns of $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ ceramic show single phase well crystallized samples from superconducting 2212 system BSCCO (Fig.1-a). The refined unit cell parameters are $a = b = 5.395 \text{ \AA}$; $c = 30.714 \text{ \AA}$, with tetragonal unit cell volume $V_m (\text{BSCCO}) = 893.962 \text{ \AA}^3$.

As seen from Fig.1b, after the treatment of BSCCO ceramic samples with the alkaline solution (7M KOH), all peaks of the super conducting 2212-type phase remain practically unchanged and no impurity phases related to the sample deterioration or phases product of the reaction with potassium hydroxide are found. Those results suggest that no phase changes in the semiconducting BSCCO ceramic occur after prolong contact of the samples with a strong alkaline solution.

Fig 1: X-Ray Diffraction Patterns (XRD) of BSCCO Ceramic Samples Before (a) and After (b) Treatment in the Alkaline Solution



The SEM images of BSCCO ceramic samples before and after alkaline treatment are presented on Fig.2. It is seen that a typical polycrystalline structure is achieved after sintering of the sample. The grains are relatively large (5-10 μm) without specific shape. After treatment in the alkaline solution no essential changes in the bulk morphology of the BSCCO samples are observed (Fig.2b).

Those observations are confirmed by EDX results summarized in Table 1. The slight changes of the content of some elements in the samples after treatment are not indicative for a chemical interaction of the ceramic with the alkaline solution. The traces of potassium, originating from the solution, are also not detected on the sample surface. It is important to note that the study of superconducting properties has shown that the superconducting critical temperature ($T_c = 109\text{ K}$) of BSCCO ceramic remains unchanged after alkaline treatment. Thus, BSCCO ceramic samples seem to remain stable after prolong treatment in 7M KOH solution (basic electrolyte for alkaline nickel-zinc batteries) and the stoichiometry of superconducting phase unchanged.

The results obtained by XRD, SEM and EDX observations and measurements of superconducting properties of BSCCO samples prove the high chemical resistance of the superconducting ceramic $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ in highly alkaline media and suggest the possibility of applying this type ceramic as an additive to the electrode materials in alkaline batteries.

Fig 2: SEM Micrographs of BSCCO Ceramic Samples before (a) and after (b) Alkaline Treatment

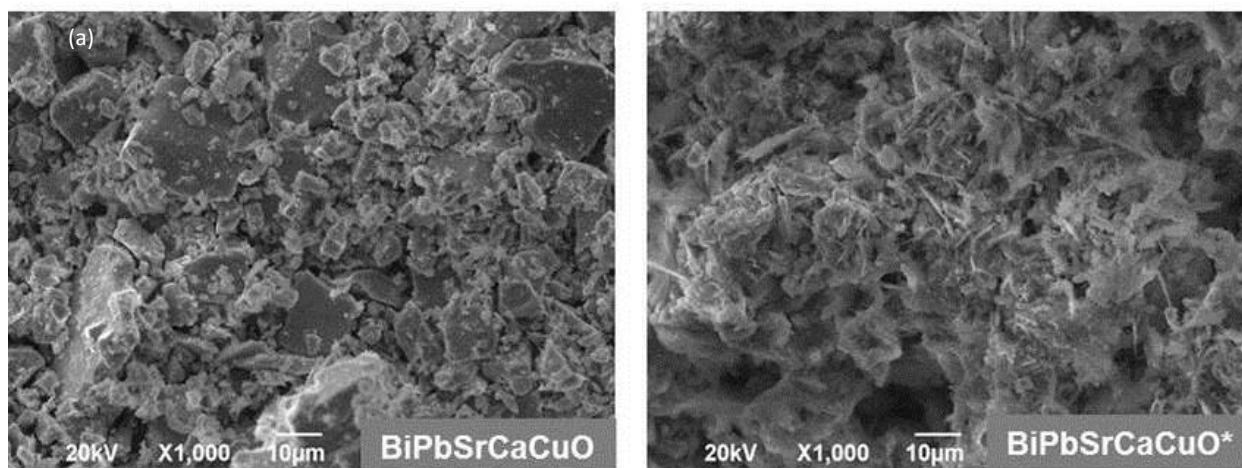


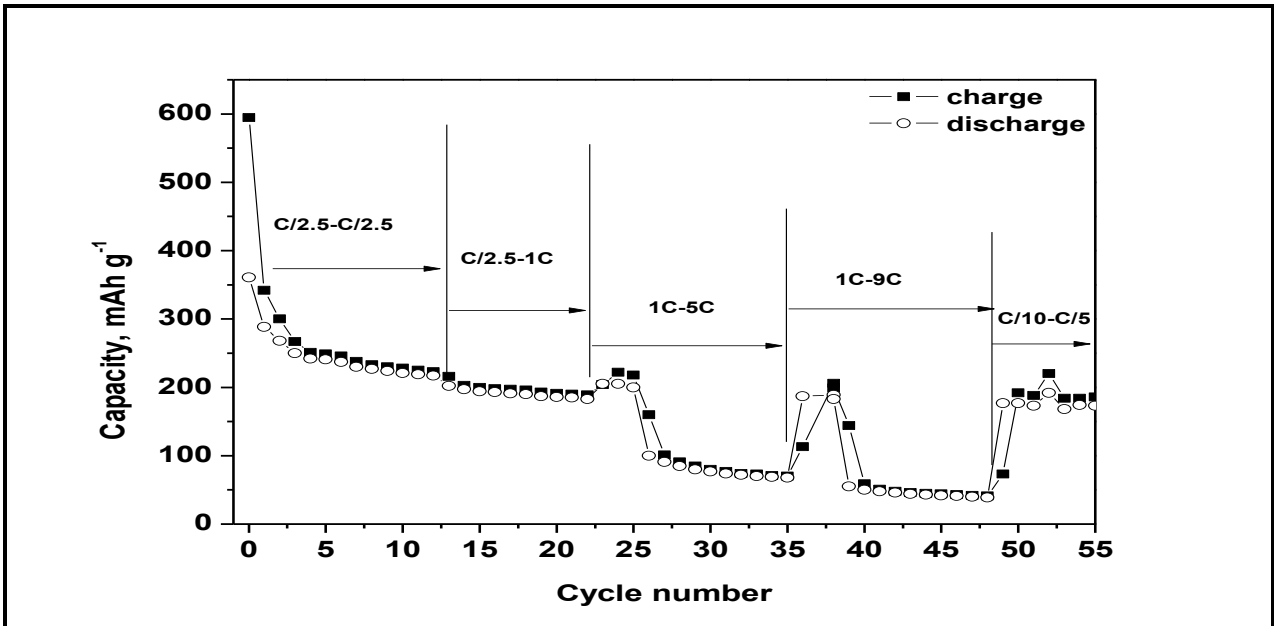
Table 1: EDX Results for Elements Content of the BSCCO Ceramic Samples Before and after Alkaline Treatment

BSCCO Ceramic Samples	Bi, at. %	Pb, at. %	Sr, at. %	Cu, at. %	Ca, at. %	O, at. %	K, at. %
Before alkaline treatment	10.17	0.54	9.35	13.06	8.52	58.36	0
After alkaline treatment	9.28	0.86	8.35	12.44	8.19	60.88	0

3.2. Electrochemical Testing of Zinc Electrodes in the Experimental Ni-Zn Battery Cells

The dependences of specific charge and discharge capacity of the zinc electrode with addition of BSCCO ceramic on the number of cycles at different current loads (according to the testing program employed) are presented on Fig. 3, while on Fig. 4 are compared the dependences of the specific discharge capacity (average values of at least 10 charge-discharge cycles at every current load) of the zinc electrode with addition of BSCCO ceramic and zinc electrode with carbon (acetylene black) conductive additive on the current load. The dependences of the specific discharge capacity for both type of zinc electrodes on the number of charge-discharge cycles at prolong cycling (up to 500 cycles) are compared on Fig. 5.

Fig 3: Dependence of the Specific Charge and Discharge Capacity of the Zinc Electrode with Addition of BSCCO Ceramic on the Number of Cycles at Different Current Loads



All data in the figures illustrate well the very good characteristics of the zinc electrode developed – higher specific discharge capacity (up to two times) in comparison the zinc electrode with “classic” carbon additive to active mass, especially at high current load (above 1C), high charge/discharge efficiency (95-98 %), good cycleability and stability of the capacity at prolonged cycling.

Fig 4: Dependence of the Specific Discharge Capacity of the Zinc Electrodes with Addition of BSCCO Ceramic and Carbon on the Current Load

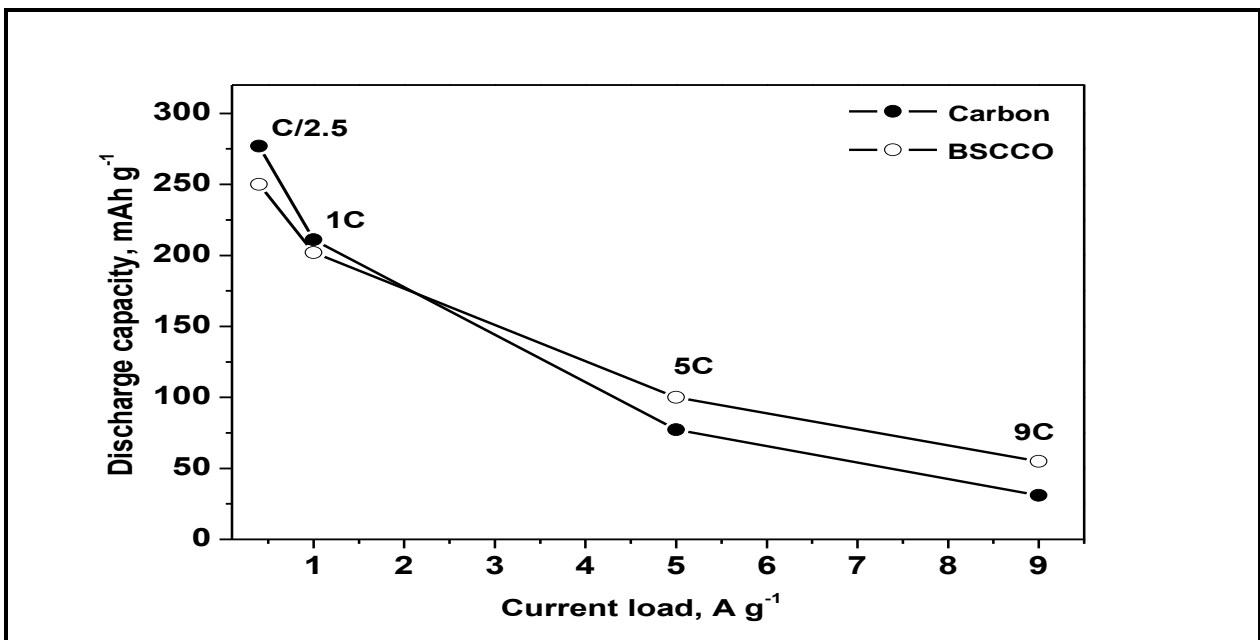
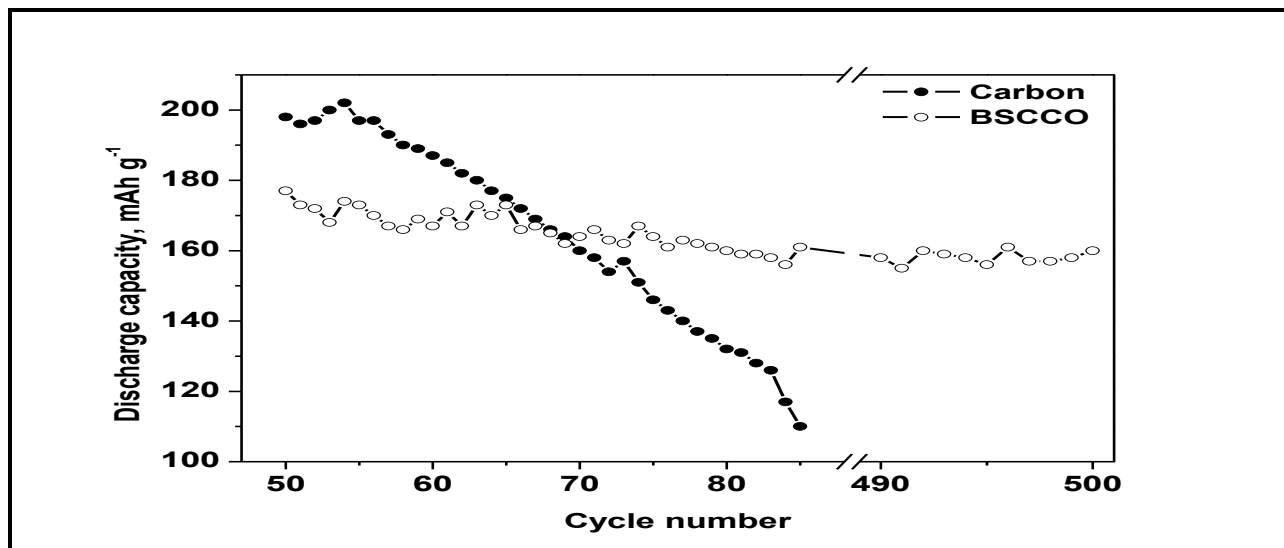


Fig 5: Dependence of the Specific Discharge Capacity of the Zinc Electrodes with Addition of BSCCO Ceramic and Carbon at Current Load C/5 (0.2 A)



The measurements of the electric resistance of the composite electrode masses have shown that the resistance of the zinc electrode mass with addition of $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ ceramic (230 ohm.cm) is about 30% lower than the resistance of the electrode mass with carbon additive (330 ohm.cm).

The results of the electrochemical studies show that the nickel-zinc battery cell with zinc electrode with active mass containing superconducting BSCCO ceramic additive exhibits generally good cycling operation ability and performance stability at prolong charge-discharge cycling. It is suggested that the superconducting powder forms a highly conductive network between the particles of the zinc oxide in the electrode mass, thus improving the electric contact in the power generation material of the zinc electrode. The addition of BSCCO ceramics improves not only conductivity and electrochemical homogeneity of the electrode mass and reduces the gas evolution (because of the absence of carbon materials with low-overvoltage of hydrogen evolution) but also stabilizes its porosity structure.

3.3. Conclusion

Powder superconductive cuprate ceramic $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ of BSCCO 2212 system is produced by solid-state synthesis and physicochemically characterized. The chemical stability of BSCCO ceramics in alkaline medium of the Ni-Zn battery is confirmed by structural and morphological analysis (XRD, SEM and EDX) and evaluation of superconducting properties of samples before and after prolong exposure to 7M KOH. The electrochemical tests are carried out by a specially designed prismatic alkaline Ni-Zn battery cell with conventional sintered type nickel electrodes and pasted zinc electrode with active electrode mass based on ZnO with addition of BSCCO powder or carbon (acetylene black) as conductive additives. It is shown that the zinc electrode with BSCCO ceramic additive exhibits very good cycleability, remarkable capacity stability and much higher discharge capacity at prolong charge/discharge cycling in comparison to the zinc electrode with “classic” carbon conductive additive. It is suggested that the addition of BSCCO ceramics improves not only conductivity and electrochemical homogeneity of the electrode mass and reduces the gas evolution but also stabilizes its porosity structure. The results obtained prove the possibility of application of superconducting BSCCO ceramics as a multifunctional additive to the active mass of the zinc electrodes for alkaline nickel-zinc battery systems.

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