The use of high-temperature superconducting cuprate as a dopant to the negative electrode in Ni-Zn batteries

A. K. Stoyanova-Ivanova[1]*, S. D. Terzieva[1], G. D. Ivanova[2], M. A. Mladenov[2],
D. G. Kovacheva[3], R. G. Raicheff[2], S. I. Georgieva[4], B. S. Blagoev[5],
A. J. Zaleski[6], V. Mikli[7]

*[1] Institute of Solid State Physics – Bulgarian Academy of Sciences,
Tzarigradsko Chaussee 72 Blvd., 1784 Sofia, Bulgaria*
*[2] Institute of Electrochemistry and Energy Systems – BAS Bulgarian Academy of Sciences,
G. Bonchev Street, bl.10, 1113 Sofia, Bulgaria*
*[3] Institute of General and Inorganic Chemistry – Bulgarian Academy of Sciences,
G. Bonchev Street, bl.11, 1113 Sofia, Bulgaria*
[4] University of Chemical Technology and Metallurgy, 8 Kl. Ohridski Blvd., 1756 Sofia, Bulgaria
*[5] Institute of Electronics – Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee Blvd.,
1784 Sofia, Bulgaria*
*[6] Institute of Low Temperature and Structure Research, Polish Academy of Sciences,
2 Okolna Str., 50-422 Wroclaw, Poland*
*[7] Centre for Materials Research, Tallinn University of Technology, 5 Ehitajate Str.,
19086 Tallinn, Estonia*

The chemical stability of YBCO ($Y_1Ba_2Cu_3O_{7-x}$) and GdBCO ($Gd_1Ba_2Cu_3O_{7-x}$) superconducting ceramics in an alkaline medium was studied by analyzing polycrystalline samples of the ceramics before and after exposure to an alkaline solution (7M KOH), normally used as a basic electrolyte in alkaline batteries. The high chemical resistance of the ceramics to the alkaline medium was confirmed by structural observations and magnetic measurements. The powder of YBCO ceramics was also used as a conducting additive to the active mass of zinc electrodes in an experimental nickel-zinc alkaline battery. The electrochemical studies were carried out by a specially designed electrochemical cell with demountable "coin" type zinc and nickel electrodes. The tests showed that the cells with an YBCO superconducting ceramic additive to the zinc electrode exhibited good cyclic operation ability and a capacity stability, as well as a higher specific capacity (by about 30%) than the cells with a zinc electrode with carbon as a conducting additive to the active mass. The results obtained suggest a possible application of these structural type superconducting ceramics as additives to the electrode material of zinc electrodes for alkaline battery systems.

Key words: Superconducting ceramics; alkaline battery; microstructure; stability

INTRODUCTION

Since the discovery of the high-temperature superconductors (HTS) in the late 1980s, the technological research has been focused on producing HTS materials in sufficient quantities to make their use economically viable and on optimizing their properties in relation to a wide range of advanced applications. The basic areas of applications of the high-temperature superconductors are divided into three general purposes [1]: bulk superconductors, superconducting tapes and wires. Bulk HTS have been developed for electronic power application as well as for magnetic separation in water cleaning systems [2].

The chemical stability and the interaction of the HTS with the environment is one of the important factors that can hinder or support their application. The deterioration of the superconducting properties of the YBCO ($Y_1Ba_2Cu_3O_{7-x}$) and BSCCO ($Bi_2Sr_2Ca_2Cu_3O_{7-x}$) systems due to the reaction with water has been studied intensively [3, 4]; it was shown that the superconductors are destroyed in a

* To whom all correspondence should be sent:
E-mail: e-mail: aksi_bg@abv.bg

few minutes by boiling water [5]. The first electrochemical investigations on the dissolution behavior of superconducting oxides were published by Rosamilia et al. [6]. The corrosion behavior of the HTS in different aqueous solutions has also been studied by cyclic voltammetry at temperatures higher than T_c in order to determine the effective exposure "lifetimes" [7]. Applying electrochemical dc and ac methods, Bachtler and Lorentz [8] found that the high temperature superconductor $YBa_2Cu_3O_{7-x}$ does not act as a special electrocatalyst for anodic oxygen evolution reaction. Moreover, the surface structure and composition of the semiconductors were found to depend strongly on the polarization conditions and the contact time with the solution.

Along with the development of zinc electrodes for alkaline battery systems, the application of different conducting powders as additives to the active electrode mass based on zinc oxide have come into consideration because of their low electronic conductivity [9]. In this respect, it is interesting to investigate the possibilities of application of different superconducting ceramic materials as additives to the electrode mass of the zinc electrodes in alkaline rechargeable battery systems, thus contributing to a longer battery life by improving the conductivity and electrochemical homogeneity of the anode mass and reducing gas evolution problems during charging of the cell.

In the present work, the changes of elemental and phase composition, as well as of the superconducting properties of samples of superconducting ceramics $YBa_2Cu_3O_{7-x}$ (YBCO) and $GdBa_2Cu_3O_{7-x}$ (GdBCO) after exposure to a concentrated alkaline solution, were first studied in order to evaluate the stability of the ceramic materials in electrolytes normally used in the alkaline batteries. Second, the behavior of the conducting ceramic powder of the high temperature superconducting system $YBa_2Cu_3O_{7-x}$ was also studied as an additive to the zinc anode mass of nickel-zinc alkaline rechargeable batteries to form a highly conducting network between the particles of the electrode mass thus improving the electrochemical contact in the power generation material in the system.

MATERIALS AND METHODS

Samples preparation

YBCO and GdBCO samples were prepared by the standard solid state synthesis. The appropriate amounts of high purity (all 99.99% pure) powders of Y_2O_3, Gd_2O_3, $BaCO_3$ and CuO were mixed, ground, pressed into pellets and subjected to sintering in three stages in an oxygen atmosphere. The first sintering was performed at 900 °C for 21h in flowing oxygen. After grinding, the powder was sintered for a second time at 930 °C under the same conditions, followed by a slow cooling and an additional annealing at 450 °C for 2h. The pellets were then pressed at 6 MPa and sintered for the third time at 950 °C for 23h, and subsequently annealed at 450 °C for 23 h.

The pellets of the sintered ceramics (10 mm diameter, 2 mm thick) were first soaked in a model alkaline solution (7M KOH) and then exposed to the same solution for 24, 48, 72 or 96 hours. After the exposure, the samples were removed from the solution, dried at room temperature and studied. Since the properties of all samples varied practically negligibly with the exposure period, further in the paper results from the longest soaking time (96 hours) are only presented and discussed

Pasted zinc electrodes and battery assembling

The pasted zinc electrodes used in the present study were prepared by inserting a preliminarily prepared zinc paste on a metal support and current collector (copper mesh). The paste was composed by powder ZnO (average particle size 30−40 nm, 88 wt.%), a conducting additive – superconducting ceramic powder YBCO (particle size 5−10 μm, 7 wt.%) and binding agents – plytetrafluorethylene (PTFE, 4 wt.%) and carboxymethylcellulose (CMC, 1 wt.%). The paste was uniformly spread on the preliminarily configured copper support (15 mm diameter). The pasted electrode was dried at 90 °C for 2 hours, then pressed under 30 MPa for 2 min and sintered at 320 °C for 10 min. For comparison, similar zinc electrodes with an active paste composed by the same nanosized ZnO (93 wt.%), the same binding agents – plytetrafluorethylene (PTFE, 4 wt.%) and carboxymethylcellulose (CMC, 1 wt.%), but with a conducting carbon additive – acethylene black (AB, 2 wt.%) were also fabricated applying the same technological procedure.

Sintered-type nickel electrodes with a nominal capacity twice as high as the capacity of the zinc electrodes were used as cathodes in the experimental nickel-zinc battery cells. A solution of 7M KOH saturated with ZnO was used as a battery electrolyte. Before assembling the cell, the electrodes were soaked under vacuum with the electrolyte for 10 min. The cell package consisted of two disk-type zinc and nickel electrodes with a diameter of 15 mm, separated by a micro porous separator (Celgard 3501). The electrode package was assembled into a coin-type cell container made of transparent material and soaked with the electrolyte. The zinc electrodes were characterized by the charge-discharge cycling behavior and the cycling life.

Methods for analysis

The X-ray diffraction patterns of the superconducting powder samples were obtained within the range 5.3 to 80° 2θ at a constant step of 0.02° 2θ on a Bruker D8 Advance Diffractometer with Cu Kα radiation and a LynxEye Detector. The phase identification was performed by a Diffracplus EVA v. 15 program using the ICDD-PDF2 (2009) Database. The mean crystallite size was determined by the Topas v.4.2 software package using the fundamental parameters peak shape description including appropriate corrections for the instrumental broadening and difractometer geometry [10].

The microstructure of the samples was studied by means of a Zeiss EVO MA-15 scanning electron microscope (SEM) with a LaB_6 cathode on the polished cross-section of the samples. The chemical composition was determined by X-ray microanalysis using energy dispersive spectroscopy (EDS) on an Oxford Instruments INCA Energy system. The qualitative and quantitative analyses were carried out at an accelerating voltage of 20 kV.

The non-stoichiometric oxygen coefficient δ was determined by spectrophotometry based on the absorbance measurement of colored Cu(II)-EDTA and Co(III)-EDTA complexes [11]. The samples were dissolved in the presence of chloride ions, Co(II) and EDTA without removing the air from the solution (pH = 2.5). Co(III)-EDTA and Cu(II)-EDTA complexes were formed in a medium of sodium acetate-acetic acid buffer (pH = 4.9) and their absorbance was measured. The δ non-stoichiometric oxygen coefficient was calculated as the ratio of the concentrations of Co(III)-EDTA and Cu(II)-EDTA complexes using salts CoF_3 and $CuSO_4$ as standards for calibration.

The magnetic measurements of bulk polycrystalline superconducting samples were performed using a PPMS (Physical Property Measurement System – Quantum Design) as follows: 1) magnetization vs. magnetic field ($-9\div9$ T) $M(H)$ measurements at a temperature of 10 K; and 2) AC magnetization (ACM) vs. temperature ($10\div200$ K) measurements in an applied AC magnetic field with a frequency of 3333 Hz and an amplitude of 0.5 mT. For the ACM measurements, the sample was first cooled down to 10 K without a magnetic field.

The electrochemical investigation of the zinc electrodes was carried out on a specialized electrochemical equipment (Arbin Instrument) allowing a galvanostatic mode charge/discharge cycling, as well as a mixed mode constant current/constant voltage cycling. The charge/discharge cycling tests were performed at room temperature. The cells were charged at 20 mA (C/5, where C = 100 mAh is the nominal capacity of the zinc electrode) for 6 h, and

then discharged at the same current load down to 1.3 V cut-off, recording the cell voltage as a function of time. Both the charge and discharge specific capacities were automatically calculated so that the important dependency of the discharge capacity of both type zinc electrodes on the number of the cycles was thus obtained.

EXPERIMENTAL RESULTS AND DISCUSSION

The X-ray diffraction patterns showed that the single-phase well-crystallized samples formed superconductive 123 systems (YBCO and GdBCO). The refined unit cell parameters were $a = 3.8209(5)$ Å; $b = 3.8938(8)$ Å; $c = 11.675(2)$ Å for YBCO (SG: Pmmm) and $a = 3.8439(5)$ Å; $b = 3.8923(7)$ Å; $c = 11.712(1)$ Å for GdBCO (SG: Pmmm) respectively, leading to a unit cell volume V_m (YBCO) = 173.70(5) $Å^3$ and V_m (GdBCO) = 175.35(5) $Å^3$. After the treatment with the alkaline solution, all peaks of the 123-type phase remained and no impurity phases related to sample deterioration or products of reaction with potassium hydroxide were found (Fig. 1). No significant changes of the unit cell parameters and the volume after the alkaline treatment were registered; however, the XRD pattern of the treated GdBCO samples showed the presence of an amorphous component, probably due to some surface structure deterioration.

It is well known that the oxygen content is crucial for the phase stability of the cuprate superconductors. Its precise control, as well as the determination of the oxygen non-stoichiometry, provides important information on the phase relation, structural defects and fundamental material properties [12, 13]. In order to obtain more detailed information about the stability of the superconducting phases of the samples treated, the oxygen content was also determined.

The average results for the non-stoichiometric coefficient δ of all (as synthesized and after exposure to the alkaline solution) YBCO and GdBCO samples obtained by spectrophotometry are listed in Table 1. Each result is the mean value of at least three independent determinations, the standard deviation being within ±0.002. The spectrophotometric method based on the absorbance measurement of the I^{3-} – starch compound was used for comparison [14]. The results obtained by the two methods practically did not differ.

Figure 2 presents SEM images of YBCO and GdBCO samples before and after alkaline treatment. It is seen that a highly homogeneous ceramics was produced after sintering the YBCO bulk sample. The grains were relatively large (5−10 μm) without
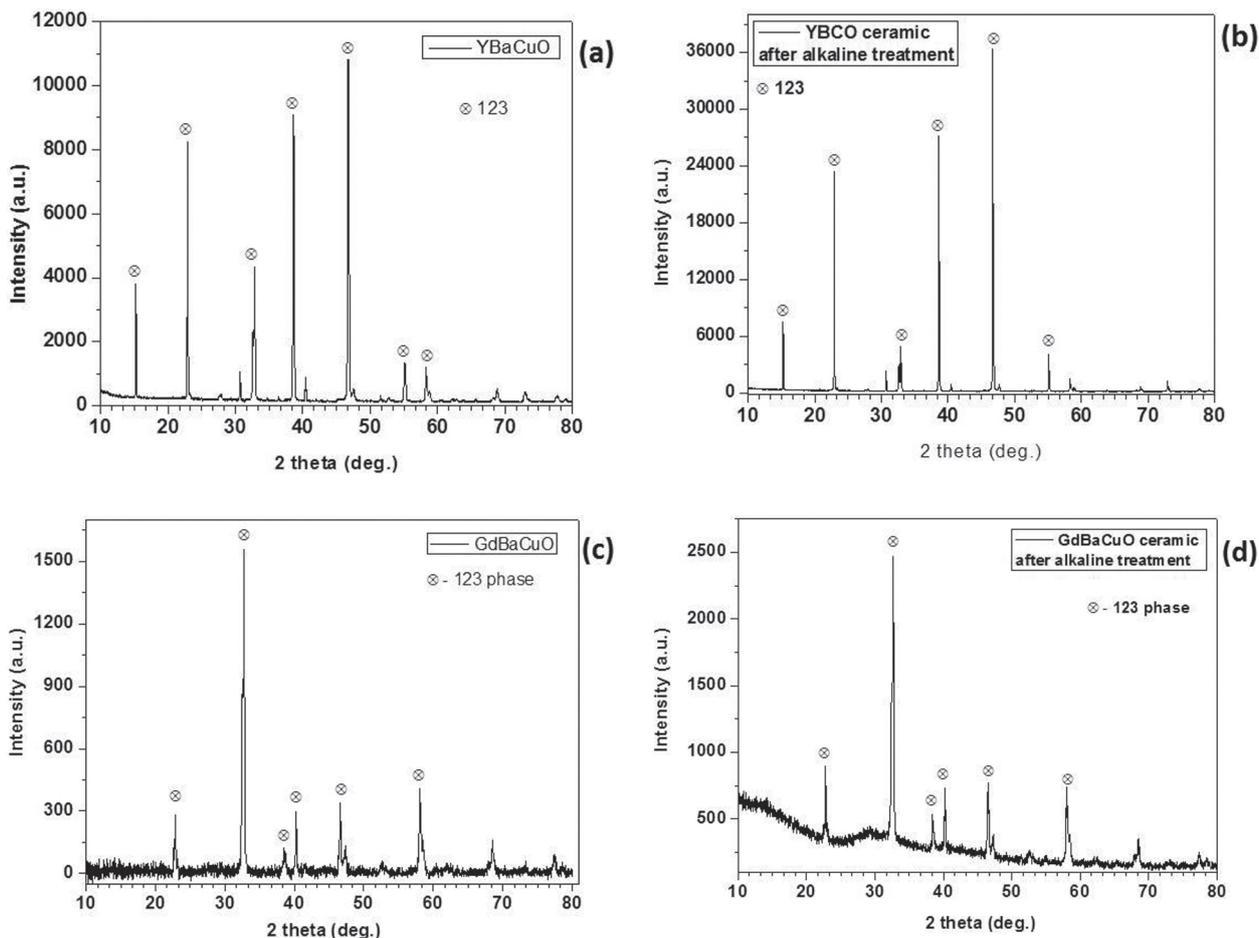
Fig. 1. Powder X-ray diffraction patterns of YBCO and GdBCO ceramic samples before (a, b) and after (c, d) alkaline treatment

Table 1. Values of oxygen coefficients "δ" and "y" as determined by spectrophotometry.

Sample	oxygen coefficient δ^*	oxygen coefficient $y = 6.5 + \delta$
YBCO	0.450	6.950
YBCO* (alkaline treatment)	0.498	6.998
GdBCO	0.376	6.876
GdBCO* (alkaline treatment)	0.387	6.887

*Each result is a mean value of at least three parallel determinations. The confidence interval with P=0.95 for each sampleis± 0.004.

a specific shape. In contrast, despite that the synthesis regime was the same for both powders, the polycrystalline GdBCO sample exhibited larger grains than the YBCO sample. After the alkaline treatment

of the ceramics, no significant changes of the bulk morphology were observed, as seen in Fig. 2.

Figure 3 shows the surface of the YBCO sample after the alkaline treatment. It is seen that this sample endured well the alkaline treatment and only small spots on the surface were changed. On the contrary, the SEM micrographs of GdBCO sample show a modified surface morphology as a result of interaction with the KOH solution. It should be mentioned that the surface changes observed concerned only a thin surface layer of the sample, while preserving the sample volume unchanged. This observation is confirmed well by the EDX results of both samples, as summarized in Table 2 and Table 3 for the YBCO and GdBCO ceramics, respectively.

The results in Table 2 indicated that YBCO samples remained stable after alkaline treatment and the stoichiometry of superconducting phase was unchanged. Only traces of potassium, originating from the solution, were detected on the sample surface.

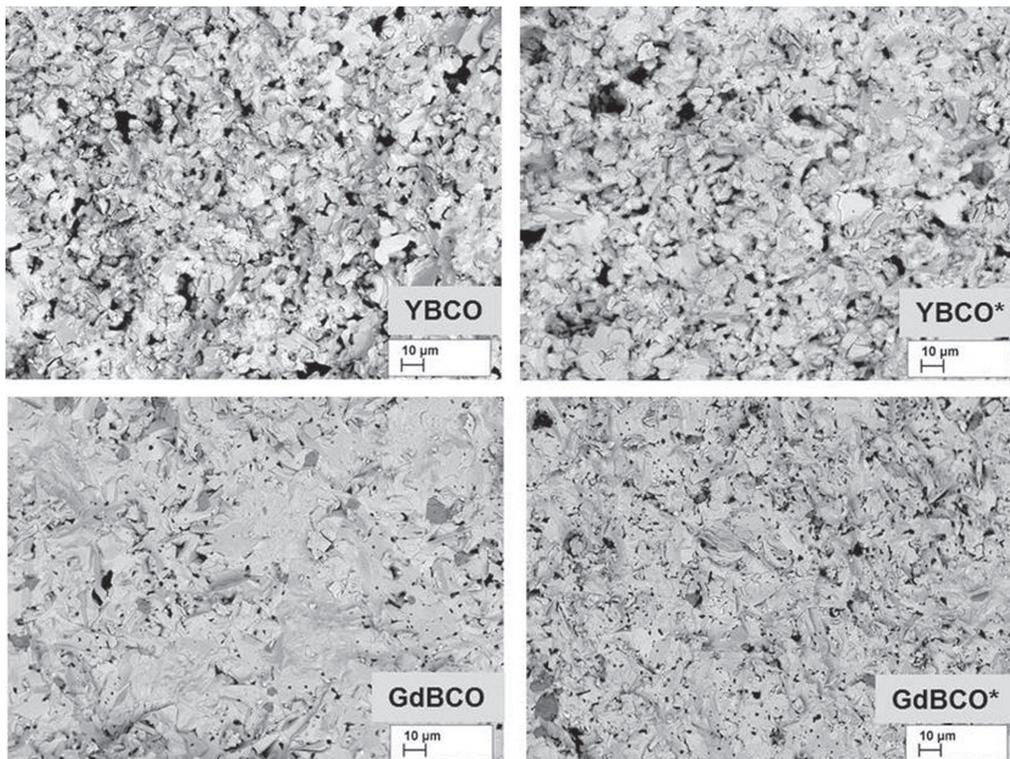The results of the EDX analyses of the GdBCO samples showed generally that the Gd-

Fig. 2. SEM micrographs of YBCO and GdBCO ceramics before and after (*) alkaline treatment
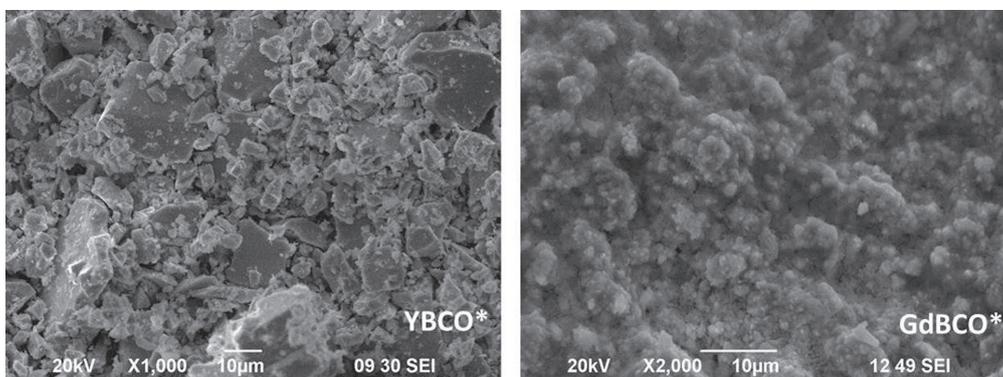

Fig. 3. SEM micrographs of YBCO and GdBCO ceramics surfaces after alkaline treatment

superconducting phase was not as stable in a highly alkaline medium as the Y-containing superconducting ceramics. The slight change of the stoichiometry observed indicated a reaction with the KOH solution and, as a result of such a reaction, parts of the barium and copper contents of the sample were lost. The changes in the chemical composition of the Gd-ceramics probably affected some physical properties of this material, as can be seen below.

The superconducting properties of the ceramics samples were studied using the AC susceptibility method. The YBCO samples (as sintered and treated in the alkaline solution) were typical superconductors with a critical temperatures $T_c = 91.3$ K. The transition behavior of the treated sample almost overlapped the original sintered one, as is seen in Fig. 4a. The complete hysteresis loop (magnetization vs. applied magnetic field – $M(H)$) was typical for superconductors without any essential difference between the treated and untreated samples (Fig. 4b). The critical fields determined were $H_1 = 0.25$ T and $H_2 > 9$ T.

Table 2. EDX results for elements content of the samples before and after (*) alkaline treatment for YBCO.

	Y at.%	Ba at.%	Cu at.%	O at.%	K at.%
Before alkaline treatment EDX (integral) YBCO	7.21	12.39	21.02	59.38	0
After alkaline treatment EDX (integral) YBCO*	7.18	12.67	20.90	59.12	0.13

Table 3. EDX results for elements content of the samples before and after (*) alkaline treatment for GdBCO

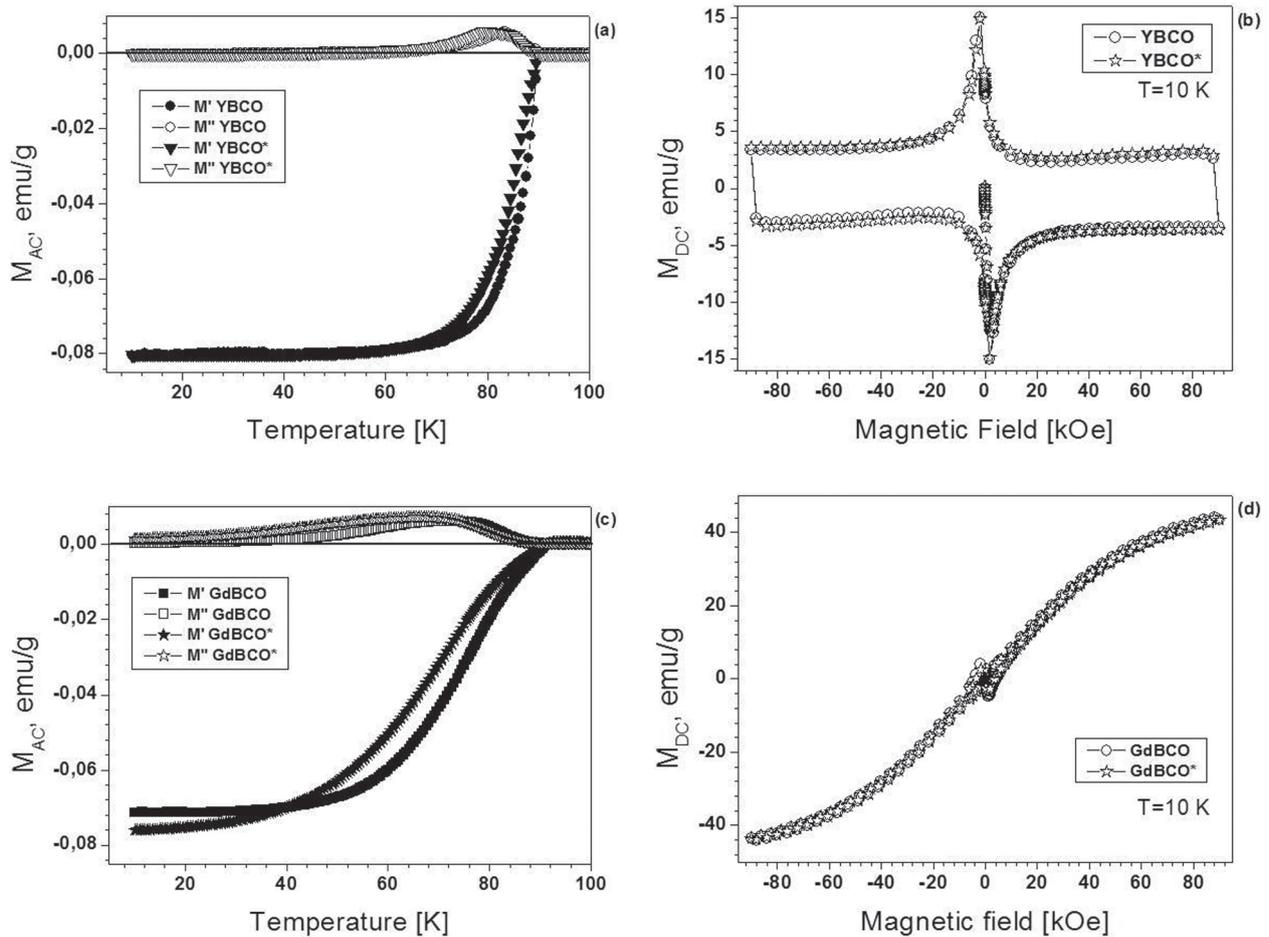|	Gd at.%	Ba at.%	Cu at.%	O at.%	K at.%
Before alkaline treatment EDX (integral) GdBCO	6.45	15.22	22.09	56.24	0
After alkaline treatment EDX (integral) GdBCO*	6.73	14.67	20.54	58.06	0

Fig. 4. The real (in-phase) and imaginary (out-of-phase) parts of the complex magnetization (ACM) vs. temperature for YBCO (a) and GdBCO (c). The hysteresis loop (magnetization vs. applied magnetic field − M(H)) for YBCO (b) and GdBCO (d)
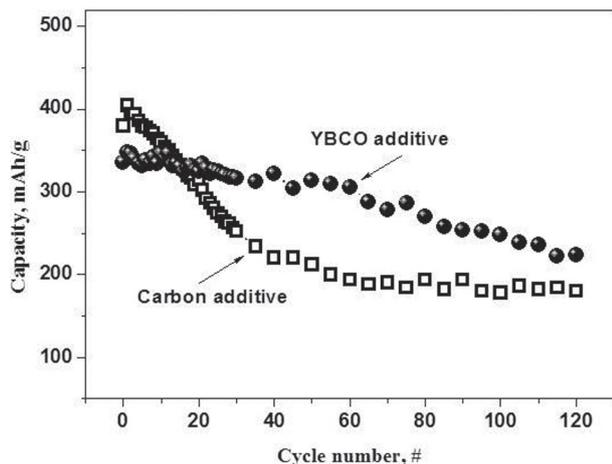
Fig. 5. Dependence discharge capacity – number of the cycles for nickel-zinc cells with zinc electrode paste containing $YBa_2Cu_3O_{7-x}$ superconducting ceramics and zinc electrode paste with carbon additive

The magnetic behavior of the sintered and alkaline-treated GdBCO samples followed the curve loops characteristic for systems with a considerable magnetic moment [15, 16]. In the case of the critical temperature measurements, some difference were observed, which could be related to a non-constant stoichiometry and the appearance of a Gd excess in the alkaline-treated sample. On the other hand, the critical parameters determined for the GdBCO ceramics were not affected significantly − only a slight decrease of the critical temperature of the alkaline treated GdBCO sample was measured as compared to the untreated one (T_c = 91.5 K for the untreated, and 91 K for the alkaline-treated sample).

Figure 5 presents typical plots of the specific discharge capacity vs. the number of cycles of the electrochemical cells with the zinc electrode paste containing carbon or $YBa_2Cu_3O_{7-x}$ superconducting ceramics as a conducting additive during the cycling test. Comparing the capacity of the cell with a zinc electrode containing superconducting ceramics with that of the cell with a zinc electrode containing a carbon additive leads to the conclusion that adding superconducting ceramics to the electrode mass maintains the cell capacity to higher values after an extended cycling.

The discharge capacity of the cell with a zinc electrode containing carbon as a conducting additive is lower (up to 30%) than the capacity of the cell with a zinc electrode containing $YBa_2Cu_3O_{7-x}$ superconducting ceramics. To summarize, the results of the electrochemical investigation showed that the nickel-zinc cell with superconducting ceramics in the zinc electrode mass exhibited generally good cyclic operation ability and a performance stability. In our opinion, the superconducting ceramic powder forms a highly-conducting network between the particles of the zinc electrode mass thus improving the electrochemical contact in the power generation material.

CONCLUSIONS

The stability of YBCO and GdBCO superconducting ceramics was investigated by analyzing polycrystalline samples before and after exposure to an alkaline solution that is normally used as a basic electrolyte in the alkaline batteries. The high chemical resistance of the ceramics to the alkaline medium was confirmed by structural observations and magnetic measurements. The study revealed that the YBCO samples are remarkably stable, while the GdBCO ceramics showed only a slight decrease of the critical temperature T_c, thus leaving the superconducting properties of the 123-type phase unchanged after the alkaline treatment.

The possibility was also studied of using the superconducting YBCO ceramics as a conducting additive to the zinc electrode mass of nickel-zinc alkaline rechargeable batteries. The electrochemical tests showed that the battery cells with an YBCO superconducting ceramic additive in the zinc electrode exhibited a good cyclic operation ability and a capacity stability, as well as a higher (by about 30%) specific capacity than the cells with zinc electrode with a "classic" carbon conducting additive to the zinc electrode mass.

The electrochemical characteristics of the experimental nickel-zinc battery cells obtained suggest that adding superconducting ceramics to the electrode mass improves the retention of the cell capacity to higher values after prolonged cycling and thus may contribute to extending the battery life.

REFERENCES

1. Narlikar, A.V; High Temperature Superconductivity 2 − Engineering Applications, Application fields of high-temperature superconductors, *Roland Hott, Springer*, Berlin, **35** (2004).

2. S. Nishijima, S. Eckroad, A. Marian, K. Choi, W. Seok Kim, M. Terai, Z. Deng, J. Zheng, J. Wang, K. Umemoto, J. Du, P. Febvre, S. Keenan, O. Mukhanov, L. D. Cooley, C. P. Foley, W. V. Hassenzahl, M. Izumi, *Supercond. Sci. Technol.*, **26**, 113001 (2013).

3. J. Dominec, L. Smrčka, P. Vašek, S. Geurten, O. Smrčková, and D. Sýkorová, *Sol. State Commun.*, **65**, 373 (1988).

4. P. Vašek, P. Svoboda, O. Smrčková, and D. Sýkorová, *Sol. State Commun.*, **71**, 403 (1989).

5. O. Smrčková, D. Sýkorová, P. Svoboda, P. Vašek, *Collect. Czech. Chem. Commun.*, **58**, 1548 (1993).

6. J. M. Rosamilia, B. Miller, L.F. Schneemeyer, J.V. Waszczak and H. M. O'Bryan, Jr., *J. Electrochem. Soc.*, **134**, 1863(1987).

7. J. T. McDevitt et al., *J. Electroanal. Chem.*, **243**, 465(1988).

8. M. Bachtler, W. J. Lorentz, W. Schindler and G. Saemann-Ischenko, *Mod. Phys. Lett. B* **2**, 6, 819 (1988).

9. H. Huang, L. Zhang, W. K. Zhang, Y. Gan, H. Shao, *Journal of Power Sources*, **184**, 663 (2008).

10. TOPAS V4: General profile and structure analysis software for powder diffraction data, *User's Manual*, Bruker AXS, Karlsruhe, Germany Bruker AXS (2008).

11. S. I. Georgieva, T. K. Nedeltcheva, L. K. Vladimirova, A. K. Stoyanova-Ivanova, *CEJC*, **11**(3), 381 (2013).

12. D. C. Harris, T. A. Hewson, *J. Solid State Chem.*, **69**, 182 (1987).

13. M. Karppinen, L. Niinisto, *Supercond. Sci. Technol.*, **4**, 334 (1991).

14. T. Nedelcheva, St. Georgieva, L. Vladimirova, A. Stoyanova-Ivanova, *Talanta*, **77**, 1745 (2009).

15. Hong Zhang, Guang Li, Tao-fei Zhou, Yong Liu, Xiao-guang Li, Yu Chen, *Chinese Journal of Chemical Physics*, **20**, 324 (2007).

16. C. H. Cheng, Chang Chun Hsieh, Chuan Ke, H. Zhang, C. C. Sorrell, *Journal of Modern Transportation*, **19**, 104 (2011).

ПРИЛОЖЕНИЕ НА ВИСОКОТЕМПЕРАТУРНИ СВРЪХПРОВОДИМИ КУПРАТИ КАТО ДОБАВКА КЪМ ОТРИЦАТЕЛНИЯ ЕЛЕКТРОД В Ni-Zn БАТЕРИИ

А. К. Стоянова–Иванова[1]*, С. Д. Терзиева[1], Г. Д. Иванова[2], М. А. Младенов[2], Д. Г. Ковачева[3], Р. Г. Райчев[2], С. И. Георгиева[4], Б. С. Благоев[5], A. J. Zaleski[6], V. Mikli[7]

[1] *Институт по Физика на Твърдото Тяло „Акад. Георги Наджаков“, Българска Академия на Науките, бул. Цариградско шосе 72, 1784 София, България*

[2] *Институт по Електрохимия и Енергийни Системи – Българска Академия на Науките, ул. „Акад. Георги Бончев“, бл.10, 1113 София, България*

[3] *Институт по Обща и Неорганична Химия – Българска Академия на Науките, ул.„Акад. Георги Бончев“, бл. 11, 1113 София, България*

[4] *Химикотехнологичен и Металургичен Университет,бул. „Кл. Охридски“ 8, 1756 София, България*

[5] *Институт по Електроника – Българска Академия на Науките, бул. „Цариградско шосе“ 72, 1784 София, България*

[6] *Институт по ниски температури и структурни изследвания, Полска Академия на Науките, ул. Околна 2, 50-422 Вроцлав, Полша*

[7] *Център за изследване на материали към Талински Технологичен Университет – Талин, Ehitajate 5, 19086 Талин, Естония*

(Резюме)

Химическата устойчивост на YBCO($Y_1Ba_2Cu_3O_{7-x}$) и GdBCO($Gd_1Ba_2Cu_3O_{7-x}$) поликристални свръхпроводими керамики в алкална среда е изследвана преди и след третиране в7М KOH разтвор, който обикновено се използва като електролит в алкалните батерии. Високата химическа устойчивост на керамиката в алкална среда е потвърдена от структурни изследвания и магнитни измервания. Керамика от вида YBCO е използвана като добавка към активната маса на цинков електрод на никел-цинкова алкална батерия. Електрохимичните изследвания са проведени в специално конструирана електрохимична клетка тип „копче“ с разглобяеми цинков и никелов електрод. Установено е, че батерийна клетка с добавка от YBCO свръхпроводима керамика подобрява стабилността на капацитета при циклиране (с около 40%) спрямо батерийна клетка с въглеродна добавка. Получените резултати дават възможност за приложение на свръхпроводими керамики като добавка към електродния материал на цинковия електрод за алкални батерии.