

**ELECTROCHEMICAL CELLS WITH ANODES PERFORMED
WITH Zn ACTIVE MASS WITH ADDED B(Pb)SCCO 2212
CONDUCTIVE CERAMICS**

Angelina K. Stoyanova-Ivanova[#], Elefteria D. Lefterova*,
Yordan G. Marinov, Galia D. Ivanova*,
Antonia E. Stoyanova*, Georgi B. Hadjichristov

Received on March 20, 2023

Presented by A. Petrov, Member of BAS, on March 28, 2023

Abstract

We studied electrochemical alkaline systems whose Zn electrodes (anodes) contain active mass produced from composites of ZnO and B(Pb)SCCO 2212 conductive cuprate ceramics. The ceramics was added at concentrations of 5, 7 or 10 wt.%. The resulting material was structurally characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). Electrochemical cells assembled with anode prepared using active mass made by employing such composites, were examined by electrochemical impedance spectroscopy. The effect from the concentration of B(Pb)SCCO 2212 ceramics on the impedimetric response and tangent loss spectra of the electrochemical cells was studied. The results show that compared to 7 wt.% and 10 wt.% concentration of B(Pb)SCCO 2212 conductive ceramics added to the Zn material of the anode, the concentration of 5 wt.% leads to lower electric losses in the assembled electrochemical cells.

Key words: conductive cuprate ceramics, Zn electrode, electrochemical cells, electrochemical impedance spectroscopy, electrical response, loss factor

[#]Corresponding author.

This work is supported by the Bulgarian Ministry of Education and Science under National Roadmap for Scientific Infrastructure (CMD No. 354 of 29.06.2017) "Distributed infrastructure of centers for synthesis and characterization of new materials and conservation of archeological and ethnographic artefacts, INFRAMAT" (Contract D01-172/28.07.2022).

DOI:10.7546/CRABS.2023.06.06

Introduction. In recent years, zinc (Zn)-based batteries have received a lot of attention as a class of promising electrochemical energy storage devices [1,2]. Such electrochemical systems are safe and offer various important advantages: high specific energy and power density; relatively low-cost electrode materials; environmentally friendly chemistry, as well as a simple recycling process of the metal recovering [3,4]. Due to the high electric conductivity and other favourable physicochemical properties, the zinc oxide is commonly used as active electrode material in Ni-Zn alkaline batteries [5–8]. In order to improve the Zn electrode performance, as well as the electrical response of such electrochemical systems, various conductive oxides and ceramics have been employed as additives to the anode active mass [9–11].

In our previous studies, conductive cuprate ceramics such as $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{CaCu}_2\text{O}_y$ (thereafter abbreviated as B(Pb)SCCO 2212, or shortly BPSCCO) were investigated as an additive to the active mass of the Zn electrode of Ni-Zn alkaline batteries. It was found that Zn active mass with included BPSCCO leads to a positive effect, in particular on the life cycles of Ni-Zn batteries [12–14], as well as on the Zn electrode conductivity [15]. The good homogeneity of the composites synthesized from BPSCCO ceramics and the other components of the Zn active mass is an important prerequisite for improving the Ni-Zn battery performance. By applying ultrasonic treatment, a fairly good homogenization of the Zn active mass containing BPSCCO at concentrations up to 10 wt.%, as well as a decrease of the electrical resistance of the electrode was achieved [13,14]. The aim of the present work is to study alkaline electrochemical systems whose Zn-electrode's active mass is prepared by including such a composite. The effect of the concentration of BPSCCO ceramic additives on the electrical response, and thereby on the electrochemical performance of such systems, was estimated. The properties of the thus modified Zn electrodes, which are closely related to their possible application in Ni-Zn alkaline systems, are established. The electrical properties of the systems were investigated in terms of complex impedance (Z^*) and tangent loss spectra.

Experimental. Materials. *Synthesis of B(Pb)SCCO 2212.* Powder samples of $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{CaCu}_2\text{O}_x$ (B(Pb)SCCO 2212) were synthesized using standard solid-state reaction from high-purity oxides of Bi_2O_3 , PbO , CuO , SrCO_3 and CaCO_3 as precursors, by mixing, grinding and initial heat treatment at 780 °C for 24 h in air atmosphere. Afterwards, the obtained mass is grinded again and the powder was sintered for 48 h at 830 °C in air.

Pasted zinc (Zn) electrodes. The ZnO nanopowder used here is commercial product of Anhui Elite Industrial Co., Ltd, Hong Kong Elite Industrial Group Limited. The Zn-electrode mass produced as a paste was composed from powdered ZnO (80 wt.%) with conducting additives – carbon (acetylene black) (either 17, 12, 10 or 7 wt.%) and B(Pb)SCCO 2212 cuprate ceramic powder (0, 5, 7 or 10 wt.%), respectively. The binding agents in the Zn paste for electrodes

were polytetrafluorethylene (PTFE, 1 wt.%) and carboxymethylcellulose (CMC, 2 wt.%). The homogenization of the synthesized Zn active masses was carried out at room temperature (23 °C) using ultrasonic treatment by 20 kHz, 1200 W lab sonicator (Hangzhou Dowell Ultrasonic Tech Co., Ltd.). Zn electrodes were designed by fine and accurate deposition and thereby inserting the Zn paste on macroporous matrix of copper foam (bulk density: 0.1–0.8 g/cm³; porosity: 50–98%) used for a carrier of the Zn mass and for current collector. The dimensions of the pasted Zn electrode layered deposits were 2.0 × 2.0 cm (thickness 1.5 mm). The pasted electrode was dried at 70 °C for 2 h and then pressed at 30 MPa for 2 min.

Methods. The produced samples of Zn-electrode active mass were structurally characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). A Philips X-ray diffractometer PW 1030 having a θ -2 θ Bragg-Brentano geometry, with Cu K α radiation (30 kV, 20 mA) with a wavelength $\lambda = 1.5406$ Å and a scintillation detector was used to determine the phase structure of the anode masses with different amount of cuprate ceramics. Diffractograms of the powder samples were obtained at room temperature and a constant scan rate and a reflection angle of 2 θ in the interval 5–90° with a step of 0.04°. The diffraction patterns obtained were interpreted by the PCPDFWIN database, ICDD, 2002. The microstructure of the electrodes prepared by use of the synthesized composite materials was characterized at ambient temperature by scanning electron microscopy (SEM) using JEOL JEM 200 CX transmission electron microscope with LaB₆ cathode. The SEM images were taken at 80 keV accelerating voltage.

Each of the investigated electrochemical cells was assembled with a copper electrode covered with a thin layer of Zn active mass – as the working electrode, a platinum plate as the counter electrode, and a calomel electrode as the reference electrode. 7 M KOH was used as the electrolyte. The ceramic-modified Zn electrodes prepared by inserting a Zn paste with a different amount of B(Pb)SCCO 2212 additive (5, 7 and 10 wt. %) into the copper foam matrix were used as a current collector and Zn mass carrier. The cell geometry was kept identical. The electrochemical behaviour of the prepared electrochemical cells was studied by electrochemical impedance spectroscopy (EIS). EIS data were acquired using an impedance-meter BioLogic SP-200. The frequency spectra of the complex electrical impedance of the assembled cells was recorded in the 1 Hz – 100 kHz frequency range of the applied alternating-current (AC) electric field (a sine-wave signal). EIS data were analyzed in terms of an equivalent circuit model using EC-Lab software.

Results and discussion. XRD patterns of powder samples of the examined material of Zn active masses are shown in Fig. 1.

It is clear that the inspected powders have a great crystallinity. The analyses of the XRD data reveal that well-crystallized single phases take place for all Zn active masses tested here. No presence of secondary phases was observed among

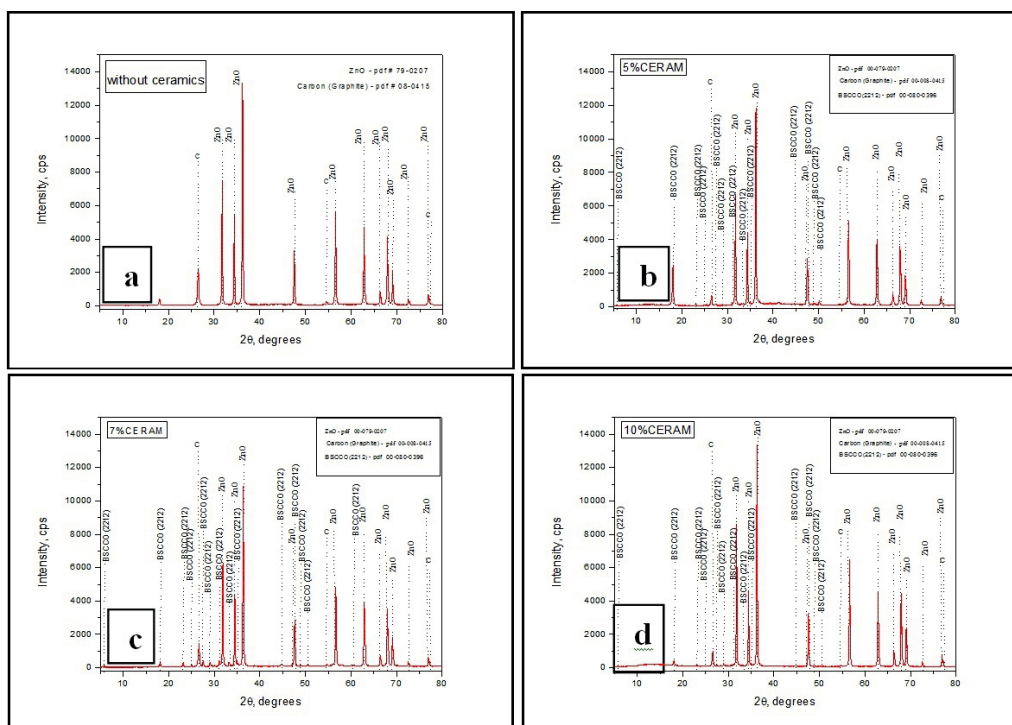


Fig. 1. Powder XRD patterns of Zn active mass containing B(Pb)SCCO 2212 ceramics at percentage: a) 0 wt.%; b) 5 wt.%; c) 7 wt.%; d) 10 wt.%

the individual samples, i.e., this structural method of investigation reveals that the mono-phase material remains also for the Zn active mass synthesized by the addition of B(Pb)SCCO 2212 ceramics.

Deposited on electrode surface, the Zn active mass prepared on identical way looked almost similar – no significant difference was visually observed on the overall area of the deposited surface. This implies a uniform distribution of the ceramic material. BPSCCO incorporated in the Zn active mass at concentrations of 5, 7 or 10 wt.% does not worsen the surface of the electrode where these composite materials were deposited.

More detailed information on the surface microstructural properties of these samples was obtained by SEM. SEM images of the samples with Zn active mass with BPSCCO (Fig. 2b, c, d) display a fairly good homogeneity, in any case better than that of electrodes on which a Zn active mass with no BPSCCO was deposited (Fig. 2a). In the latter case, a coarse morphology with nonuniform particles agglomerated in irregularly shaped structures, was observed (Fig. 2a). By adding BPSCCO, the complex 3D polycrystalline morphology in the latter becomes denser and smoother (Fig. 2b, c, d), and the deposits of the composite Zn active mass become more compact. Hence, the addition of BPSCCO significantly

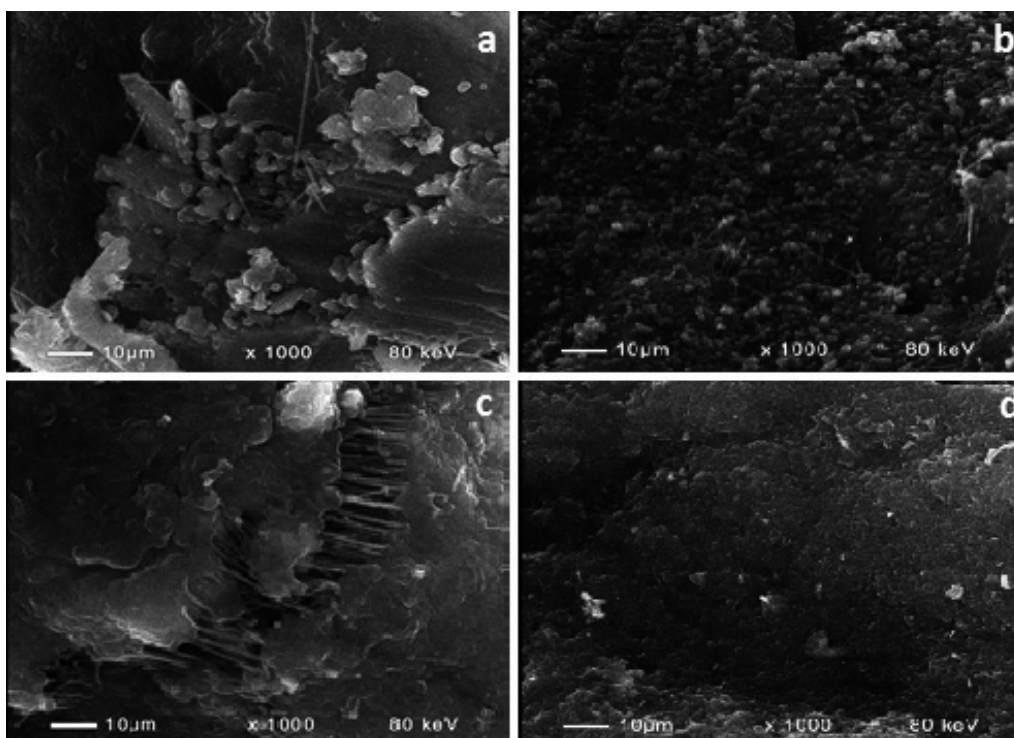


Fig. 2. SEM micrographs of electrodes prepared using Zn active mass containing B(Pb)SCCO 2212 ceramics at percentage: a) 0 wt.%; b) 5 wt.%; c) 7 wt.%; d) 10 wt.%

modifies (improves) the microstructure of the composite Zn-active mass formed on the electrode. This is most likely owing to the treatment by ultrasonic mixing of this material (paste) before its deposition on the electrode. However, some reduction in surface quality may also be possible, in particular the needle-like structural formations up to ten micrometers in length, observed for the sample containing 7 wt.% (Fig. 2c).

The SEM micrographs in Fig. 2 show a formation of a typical polycrystalline grained structure on the surface of the inspected samples (electrodes). With Zn active mass with no BPSCCO, the grains are relatively large (5–10 μm) without a distinct shape (Fig. 2a). Among the samples inspected, the sample with Zn active mass with 5 wt.% B(Pb)SCCO 2212 exhibits a fine-grained structure and a higher homogeneity of the grains distribution (Fig. 2b). These results are consistent with those obtained in our previous studies. As reported in [13,14], the ultrasound treatment affects the Zn active mass containing B(Pb)SCO 2212 additive, thus improving the surface characteristics of the deposits of these composites on electrodes made by use of copper foam. It is well known that the electrode surface area plays a key role in the performance of electrochemical systems.

The electrical properties of electrochemical systems (cells) assembled with the composed plane-parallel Zn electrodes can be estimated by applying EIS. Figure 3a, b presents the raw experimental data – the real (ReZ) and imaginary (ImZ) parts of the complex electrical impedances recorded for cells with electrodes prepared by use of the composite Zn-active mass with the three concentrations of BPSCCO. The corresponding Nyquist complex impedance plots ($-ImZ$ vs. ReZ) obtained from these data are shown in Fig. 3c. The electrical conductivity (σ) of these electrochemical systems is related to their bulk electrical resistance (R_B) through relation $\sigma = d/(R_B A)$, where A and d are the electrically-active area of the electrodes and the distance between them, respectively. The value of R_B can be determined from the (extrapolated) point of interception of the low-frequency end of the semicircle with the ReZ -axis of the Nyquist plot [16,17]. It is seen in Fig. 3a that at a lower concentrations of BPSCCO (5 or 7 wt.%), the value of σ is higher than that with electrodes having BPSCCO at 10 wt.%.

One can also compare the electric loss in the examined electrochemical cells. The electric loss tangent ($\tan \delta$), or the energy dissipation factor, is a measure of the electrical energy dissipation due to various physical processes, such as electrical conduction and loss from non-linear processes. As known, the value of $\tan \delta$ is defined as the ratio of the imaginary and the real components of the complex permittivity (ε), $\tan \delta = Im(\varepsilon)/Re(\varepsilon)$. At the parallel plate capacitor-like geometry of the cells investigated with two blocked electrodes, this expression can be transformed as $\tan \delta = ReZ/ImZ$, taking into account the relations: $Re(\varepsilon) = -ImZd/2\pi f\varepsilon_0 A|Z|^2$ and $Im(\varepsilon) = ReZd/2\pi f\varepsilon_0 A|Z|^2$ [16,17], where ε_0 is the vacuum permittivity, f is the frequency of the applied AC electric field, d and A are mentioned above.

The frequency behaviour of $\tan \delta$ calculated for the considered electrochemical systems is shown in Fig. 3d. Among the three samples examined, the cell assembled with electrode composed of Zn active mass containing 5 wt.% BPSCCO exhibits the smallest magnitude of $\tan \delta$ peak, i.e., the electric losses in this case are the lowest. Since all experimental conditions were kept the same during the EIS measurements of the three investigated cells, except for the concentration of the BPSCCO included into the Zn active mass deposited on their anode, the observed effect is obviously due to BPSCCO ceramics modifying the electrical (and dielectric) properties of this electrode. In general, the considered electrical losses are closely related to the dielectric properties ($Im(\varepsilon)$), in our case – of the composite Zn active mass, and especially the properties of the incorporated BPSCCO ceramics. As such, the electrical losses depend on the design of this material and its thermal properties, and are a function of both frequency and temperature. Furthermore, the considered losses strongly depend on the surface roughness and the boundary between the Zn active mass and the copper foam substrate of the electrode, as well as on the grain boundaries themselves [18,19]. Grain size also influences the electrical losses.

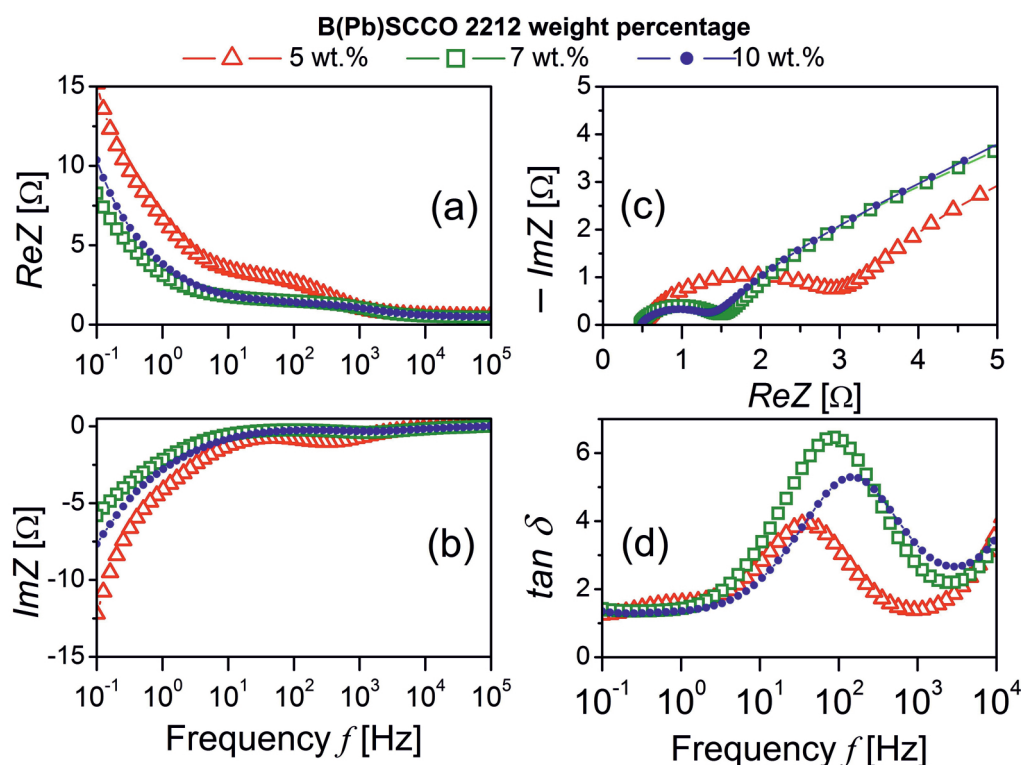


Fig. 3. Frequency spectra of real (a) and imaginary (b) part of complex electrical impedances measured for the studied electrochemical cells whose anode has a deposited Zn active mass containing B(Pb)SCCO 2212 ceramics at various concentrations (wt.%). The amplitude of the AC voltage applied on the electrodes was 10 mV (RMS); (c) Corresponding Nyquist plots; (d) Variation of $\tan \delta$ vs. electric-field frequency for the same three electrochemical cells with different compositions

The sensitivity of the impedimetric response of the examined electrochemical systems to the potential (U) applied between the working and the reference electrode (RE) can be seen in the representative example in Fig. 4a. The AC response of the electrochemical cells assembled with electrode materials studied here can be described by the equivalent electrical circuit shown in the inset in Fig. 4a. The series resistance R_s accounts for the electrical contact and/or the resistance of the electrolyte. The two overlapped and depressed semicircles in the Nyquist plot can be described with two constant phase elements (CPEs). Besides CPE1, the other CPE in the equivalent circuit (CPE_{d1}) takes place instead of capacitor because of the electrode inhomogeneity and porosity.

Analysis of the impedance spectra shows that the small subtle semicircle on the high-frequency side of the Nyquist plot (the region of the lower values of ReZ impedance) described with resistance R_p does not depend on the value of the potential applied in the course of the EIS measurements. The parameter R_p

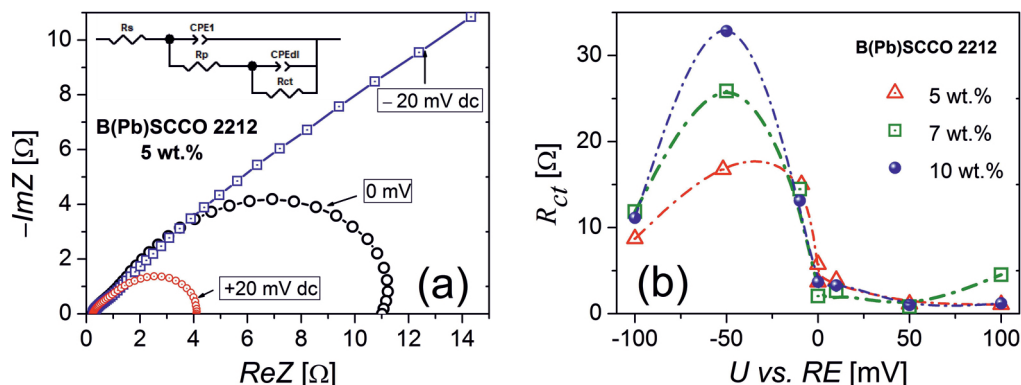


Fig. 4. (a) Nyquist impedance plots for electrochemical cell assembled with the composite Zn electrode containing 5 wt.% B(Pb)SCCO 2212 ceramics additive, at room temperature, by applying various dc potentials ($|U|$). Data obtained for three-electrode configuration (EIS measurements in potentiostatic mode). The inset: equivalent electrical circuit scheme describing the AC impedimetric response of the sample. (b) Dependence of the calculated value of R_{ct} on the applied potential (U vs. RE), as obtained from EIS measurements. The studied electrochemical cells were identical, but with anode composed with a Zn active mass containing different B(Pb)SCCO 2212 amount (5, 7 or 10 wt.%). The curved lines in the plots are spline interpolations

is associated with the net electrical resistance of the electrode, as well as with its morphology properties (homogeneity, porosity, roughness, and others). The value of R_p determined for the electrodes with B(Pb)SCCO 2212 studied here was between 1.5Ω and 1.7Ω ($\pm 0.1 \Omega$).

The enlarged semicircle for the negative potential values, e.g., $U = -20$ mV (Fig. 4a), is due to charge transfer through the double layer (CPE_{dl} – double-layer capacitor). The charge transfer resistance (R_{ct}) strongly depends on the value of the applied potential (U vs. RE). Figure 4b presents the results for R_{ct} value as obtained from analyses of EIS data for the studied electrochemical cells. The increase of R_{ct} in the range from -10 to -50 mV, as well as with the BSCCO concentration can be explained by redox processes in BPSCCO ceramics, as observed in our previous investigations on the same BSCCO ceramics used as additive to Zn electrodes in alkaline solutions, an environment similar to Ni-Zn electrochemical cells [20]. Because these processes are significant for the performance of the electrochemical system, their influence deserves to be elucidated by further electrochemical studies, including cyclic voltammetry and galvanostatic charge/discharge measurements (work in progress).

Conclusions. Composite Zn active mass (as the anode electrode material in Zn-Ni batteries) prepared by inclusion of 5, 7 or 10 wt.% of conductive B(Pb)SCCO 2212 ceramics were comparatively studied. Characterized by XRD and SEM, the electrodes prepared with use of these materials, in particular the composites with 5 wt.% B(Pb)SCCO 2212, exhibit microstructural properties that

can be suitable for their use in Zn-Ni electrochemical systems. The electrical performance of electrochemical cells assembled with anodes prepared with produced Zn active mass depends on the concentration of the ceramics added.

The analysis of the electric impedance spectra of such electrochemical systems indicated that the redox processes in them are enhanced by the increase of the concentration of the B(Pb)SCCO 2212 ceramic additives (in the range 5–10 wt.%). Significantly, at a lower concentration of B(Pb)SCCO 2212, e.g., 5 wt.%, a lower electric loss was established for the examined cells (related to the better surface properties of the layer deposited on the anode). Thus, such composite material (Zn active mass) with included B(Pb)SCCO 2212 conductive ceramics can be proper for producing electrodes in Ni-Zn electrochemical alkaline systems with enhanced performance. The results reported here are useful for optimization of such composite materials for Zn active mass containing conductive ceramics for electrodes, electrochemical systems and related devices, and are encouraging to synthesize composite Zn active mass with included new ceramic materials with improved characteristics to design anodes in Ni-Zn batteries.

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G. Nadjakov *Institute of Solid State Physics*
Bulgarian Academy of Sciences
 72 Tsarigradsko Shosse Blvd
 1784 Sofia, Bulgaria
 e-mails: angelina@issp.bas.bg
 ymarinov@issp.bas.bg
 georgibh@issp.bas.bg

**Institute of Electrochemistry*
and Energy Systems
 “Academician Evgeni Budevski”
Bulgarian Academy of Sciences
 Akad. G. Bonchev St, Bl. 10
 1113 Sofia, Bulgaria
 e-mails: e.lefterova@iees.bas.bg
 galia.ivanova@iees.bas.bg
 antonia.stoyanova@iees.bas.bg