

Influence of various preparation methods on the electrochemical properties of the active Zn mass with conductive cuprate ceramics as additives

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ABSTRACT

The subject of this research is a study of the influence of different methods (ball-mill treatment, ultrasound treatment and mechanical mixing) for obtaining Zn-electrode active mass. Zn-electrodes are prepared using ZnO, carbon and addition of two ceramics - ((Bi_{1.7}Pb_{0.3}Sr₂CuO_x (B(Pb)SCO 2201) and Bi_{1.7}Pb_{0.3}Sr₂CaCu₂O_x (B(Pb)SCCO 2212)). The phase composition and morphology of the as-prepared samples were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The conductivity of Zn-electrodes was examined by electrochemical impedance spectroscopy (EIS). It has been found that the ultrasound treatment leads to the better homogenization of the active mass with B(Pb)SCCO 2212. The observed results can be explained on one hand by the processes that take place during ultrasonic treatment and on the other hand by the presence of calcium carbonate in the ceramic, which probably favours faster processes at the micro level.

KEYWORDS: ball-mill, ultrasound and mechanical homogenization, conductive cuprate ceramics, Zn-electrode, electrochemical impedance.

INTRODUCTION

The use of ceramics as additives to the zinc electrode mass of Ni–Zn alkaline battery is known to

improve the properties and prolong the life of the battery [1].

In our previous studies, two types of B(Pb)SCCO conductive cuprate ceramics (Bi_{1.7}Pb_{0.3}Sr₂CaCu₂O_y (B(Pb)SCCO 2212) and Bi_{1.7}Pb_{0.3}Sr₂CuO_y (B(Pb)SCO 2201)) as additives to the zinc electrode mass of Ni–Zn alkaline batteries were studied [2-6] and their positive effect on the improvement of the electrochemical properties of Zn-electrode was confirmed. At and above liquid nitrogen temperatures the B(Pb)SCCO materials themselves are known to be superconductors [7]. After a prolonged exposure to highly alkaline battery electrolyte (7 M KOH), the chemical stability of the B(Pb)SCCO materials was confirmed by magnetic measurements as well as structural and surface morphology analysis of the ceramic samples [3, 4]. Good performance stability of the nickel-zinc cells with ceramics in the zinc electrode mass was confirmed by electrochemical tests [4]. An increase in the conductivity and homogeneity of the electrode mass in the presence of the used additives, as well as the formation of a highly conducting network between the zinc oxide particles were shown to lead to increased discharge capacity of the battery [2].

The results from our previous impedance studies have shown that during the charge of the electrode, reduced products are formed from the ceramic, which improves the contact between the particles of active ZnO material and the overall conductivity of the electrode. In the case of the

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B(Pb)SCCO 2212 modification the formation of Ca- and Sr- products has been found to decrease the solubility of ZnO in the electrolyte thereby suppressing the shape change of the electrode [8].

Achieving good homogeneity of the ceramic with the other components in the zinc active mass is an important prerequisite for improving the Ni-Zn battery performance. The method of electrode preparation can modify the surface morphology and therefore its correct choice has a significant effect. Several approaches have been used such as high-energy ball-milling [9], ultrasonic irradiation [10] and various combinations of methods [11]. It has also been found that the achievement of a good effect is influenced by many factors, such as processing time, the environment in which it is performed and others. For example, Rabanal *et al.* have found that the electrode characteristics of olivine-LiCoPO₄ are improved by high energy ball-milling for 1/2 h, as a lower cell polarization and a larger reversible specific capacity are observed [12].

Our previous study of zinc active mass with two ceramic additives (B(Pb)SCO 2201 and B(Pb)SCCO 2212) showed that homogenization with a ball-mill for 1 hour with steel balls does not lead to a change in it [13]. There was a slight improvement in the homogenization of the B(Pb)SCO 2201 additives and the ZnO, when an ultrasound-assisted mixing method for 3 hours was applied [10].

It is of interest to examine in more detail the structural, morphological and electrochemical changes

that might occur in the active mass and the electrodes, due to the different method of preparation: ball-milling treatment, ultrasound and mechanical (by hand) mixing. This study might prove useful in explaining how the different method of preparation might improve or worsen the homogenization of the zinc mass content and the overall performance of the Zn-electrode.

MATERIALS AND METHODS

Materials

Nine electrode active mass composites were made and then plasticized. Their composition and the used homogenization method are listed in Table 1. The used wt.% of the components for the preparation of the electrode active mass is according to a patent [5].

The ZnO nano powder used is from NZnO50, Anhui Elite Industrial Co., LTD, Hong Kong Elite Industrial Group Limited. The B(Pb)SCCO conductive ceramic were synthesized through two-stage solid state reaction and high-purity (99,99 %) oxides and carbonates (Bi₂O₃, PbO, CuO, SrCO₃ and CaCO₃) were used as starting materials.

The homogenization of the active masses was carried out at room temperature (23 °C) for 1/2 hour. The ball-mill treatment was carried out using the Fritesch apparatus. To achieve the ultrasonic treatment, an ultrasonic cleaner, model CD-3800A, with a frequency of 42 kHz was used. The mechanical mixing was performed manually.

Table 1. Used composite active masses and methods of homogenization.

Electrode	Powder ZnO, %	PTFE* %	CMC** %	Acetylene Black, %	B(Pb)SCO 2201, %	B(Pb)SCCO 2212, %	Methods of homogenization			
1 (ZnO, MT)	67	14	14	14	-	-	Mechanical			
2 (ZnO, BM)					-	-	Ball-Mill			
3 (ZnO, US)					-	-	Ultrasound			
4 (2201, MT)				7	7	7	7	-	Mechanical	
5 (2201, BM)									Ball-Mill	
6 (2201, US)									Ultrasound	
7 (2212, MT)							-	7	-	Mechanical
8 (2212, BM)										Ball-Mill
9 (2212, US)										Ultrasound

* Polytetrafluorethylene

**Carboxymethylcellulose

The electrodes used for current collectors and carriers of the zinc mass were prepared by inserting zinc paste in a 2x2x0,15 cm copper foam matrix (after which it is covered with tin and zinc). The so-prepared electrodes are then dried at 70 °C for 2 hours and then pressed under 30 MPa for 2 min.

Methods

Physicochemical (X-ray diffraction (XRD), scanning electron microscopy (SEM)) and electrochemical impedance spectroscopy (PEIS) were done on all electrodes with and without B(Pb)SCCO ceramic additives, prepared by the three different methods.

The samples were examined using a Philips X-ray diffractometer PW 1030 having a θ - 2θ Bragg-Brentano geometry, with Cu K α radiation (30 kV, 20 mA) with a wavelength $\lambda = 1.5406 \text{ \AA}$ and a scintillation detector. The original radiographs were obtained at room temperature and a constant scan rate and a reflection angle of 2θ in the interval $5 \div 90^\circ$ with a step of 0.04° . The diffraction patterns obtained were interpreted by the PCPDFWIN database, ICDD, 2002. The microstructure of the prepared active masses was studied by JOEL-200 CX scanning electron microscope (SEM) with LaB₆ cathode on the polished cross-section of the samples, at 80 keV.

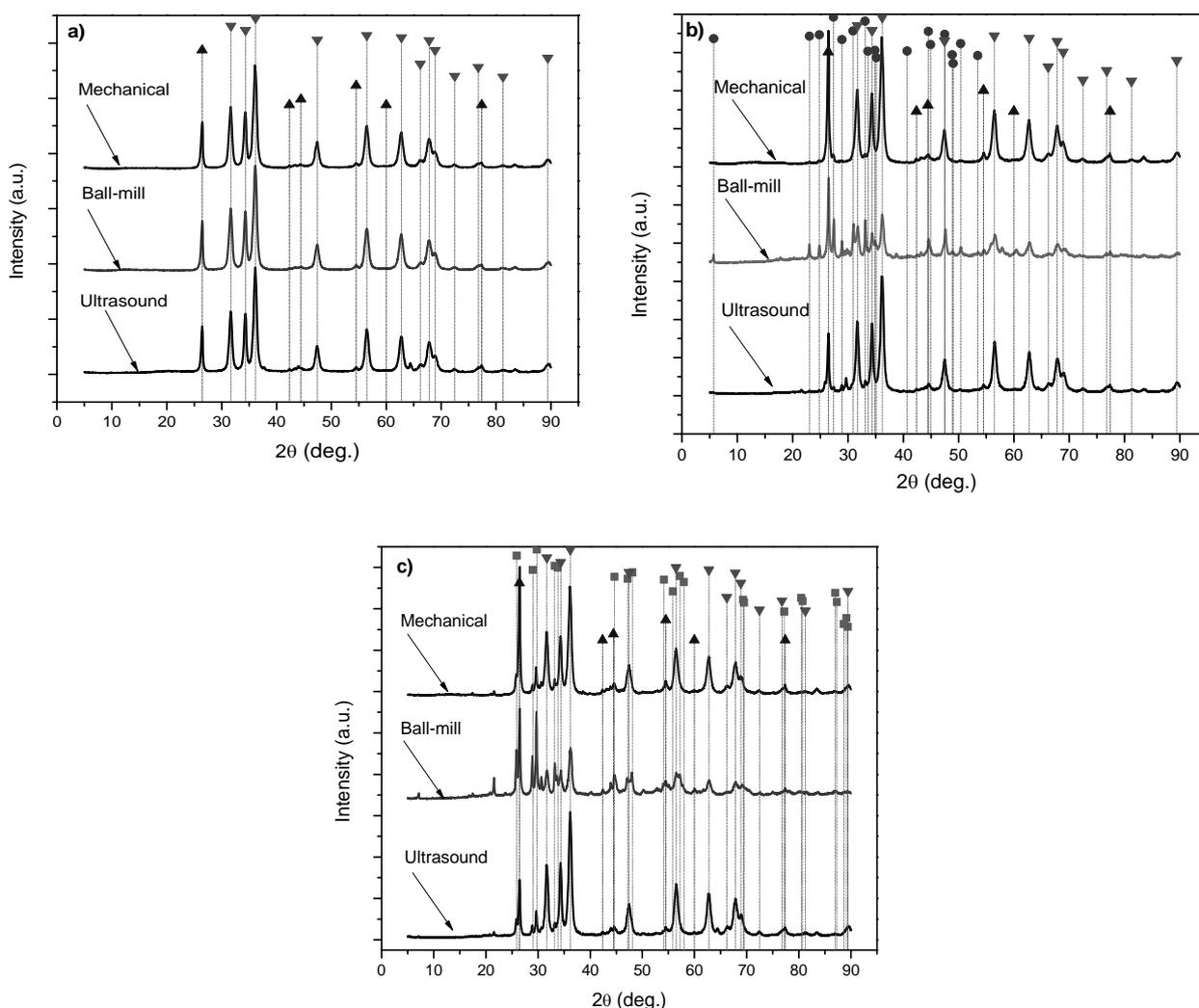


Figure 1. Comparison of the XRD spectra of the electrodes homogenized with different techniques: without conductive ceramic additive (a), containing B(Pb)SCCO 2212 (b) and containing B(Pb)SCO 2201 (c). Observed phases: ∇ - ZnO; \blacktriangle - carbon; \bullet - B(Pb)SCCO 2212; \blacksquare - B(Pb)SCO 2201.

The electrochemical system SP-200: potentiostat/galvanostat was used to perform electrochemical impedance spectroscopy (EIS) measurements. The obtained impedance spectra were fitted to an equivalent circuit model using the ZView[®] software from Scribner Associates. EIS measurements were taken using the ZnO electrodes as the working electrode (WE) in a three-electrode electrochemical cell. The counter-electrode (CE) was a platinum plate. Potential was measured relative to a saturated calomel reference electrode (RE). The applied sine-wave potential amplitude is 10 mV. In some cases a higher potential of 20 or 30 mV was required in order to obtain noise-free data. In all experiments the frequency was swept from 100 kHz

down to 0.1 Hz. The supporting electrolyte was 7 M KOH.

Impedance spectra were taken at 25 °C in order to examine the electrode kinetics in conditions near the ones of a working battery.

RESULTS AND DISCUSSION

In Figure 1 are shown powder X-ray diffraction patterns of the electrodes without and with conductive ceramic (B(Pb)SCCO 2212 and B(Pb)SCO 2201) homogenized by three different methods – mechanical, ball-mill and ultrasound.

As seen from the data shown in Figure 1 no significant difference was observed in the spectra of the electrodes, obtained by the three homogenization

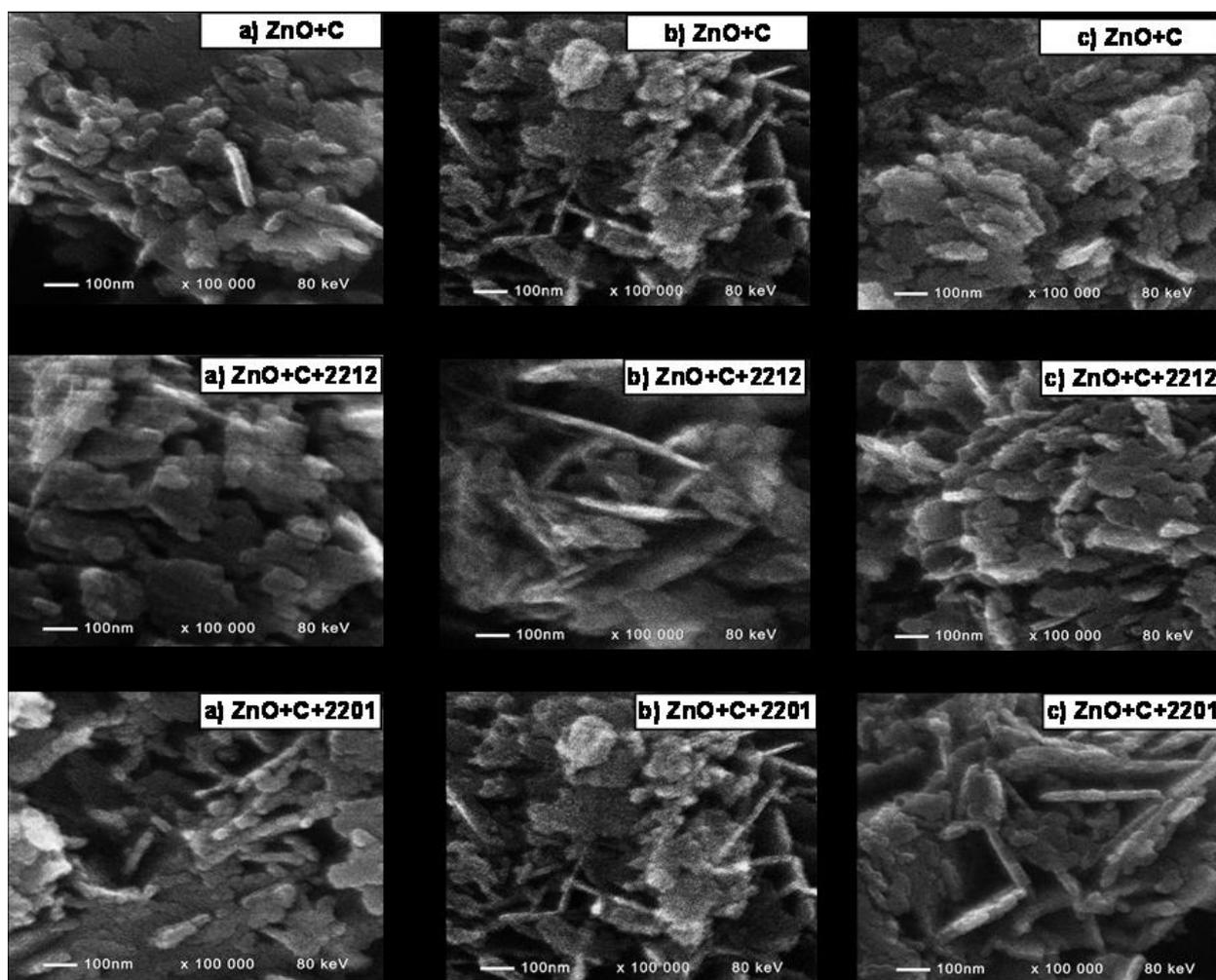


Figure 2. SEM images of the electrodes homogenized with different techniques: a) mechanical treatment; b) ball-mill treatment; c) ultrasound treatment.

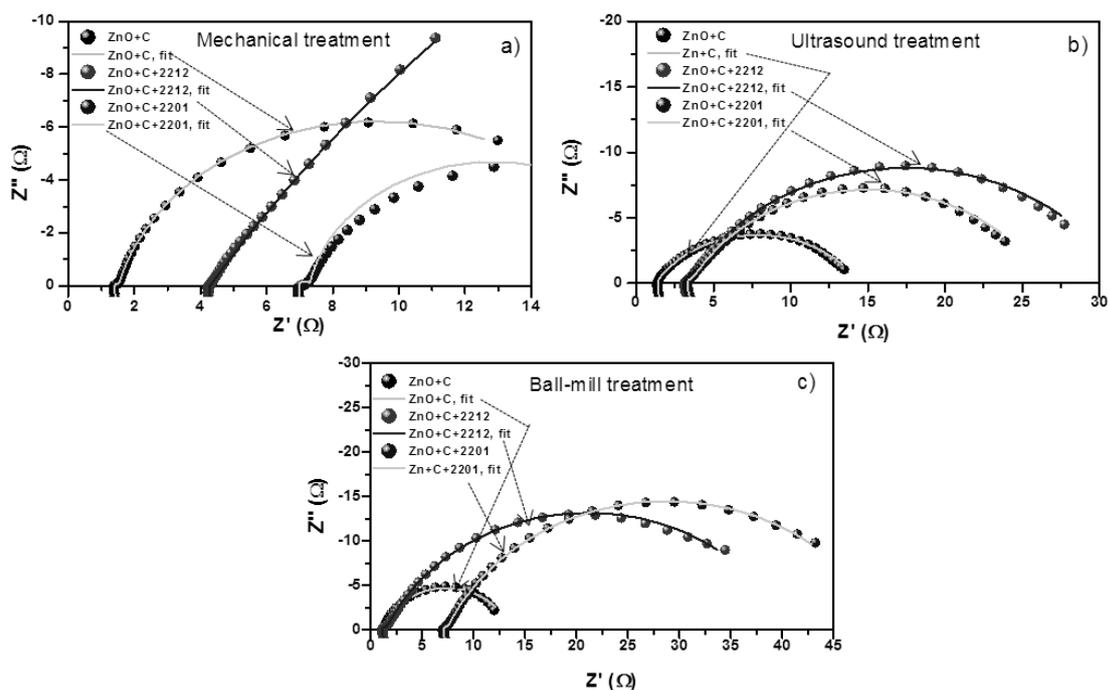


Figure 3. Nyquist impedance plot of electrode without conductive ceramic additive; with B(Pb)SCCO 2212; with B(Pb)SCO 2201 at 25 °C: **a)** mechanical treatment, **b)** ultrasound treatment, **c)** ball-mill treatment.

methods. No new phases are observed; only the intensity of the peaks of the electrodes with B(Pb)SCCO 2212 ceramics and ultrasonic treatment are slightly higher (Figure 1c).

Scanning electron microscopy was performed in order to study the effect of the treatment method on the electrode morphology (Figure 2).

Figure 2 shows that the electrodes with mechanically treated active mass are inhomogeneous and the ceramic particles are unevenly distributed (Figure 2a). Homogenization of active mass with B(Pb)SCO 2201 ceramic in ball-mill also does not have a positive effect. During these treatments the morphology of the electrodes changes and the appearance of needle-like structures is observed, which are unfavorable for the zinc electrode performances.

SEM-images show that after ultrasound-assisted mixing, better homogenization of B(Pb)SCCO 2212 and B(Pb)SCO 2201 particles in the zinc active mass is observed. The morphology of the electrode surface also changes, becoming layered (Figure 2c). These results correlate well with those of our previous studies according to which ultrasound treatment mainly affects the active mass with B(Pb)SCO 2201 additive [10].

Electrochemical impedance spectroscopy (EIS) measurements were taken in a wide frequency range (100 kHz - 0.1 Hz) in a three-electrode electrochemical cell. The electrodes listed in Table 1 were used as working electrodes.

Nyquist and Bode impedance plots of different electrodes and techniques are presented in Figure 3 and Figure 4.

The Nyquist plots (Figure 3) are typical for porous electrode and such impedance spectra are described and fitted with Randle equivalent circuit presented in Figure 5. The inductance L is due to the electrical cables and R_s - to contacts, cables and electrolyte resistances. The lack of homogeneity leads to the semicircle suppression and in this case the capacitor is replaced by constant phase element (CPE). The high frequency process described with R_1 and CPE1 is explained with electronic resistance of the electrode, and/or ionic resistance in the pores. The second arc is connected with charge transfer through the electrode/electrolyte interface with parameters charge transfer resistance R_2 and double layer capacitance -CPE2 [14, 15].

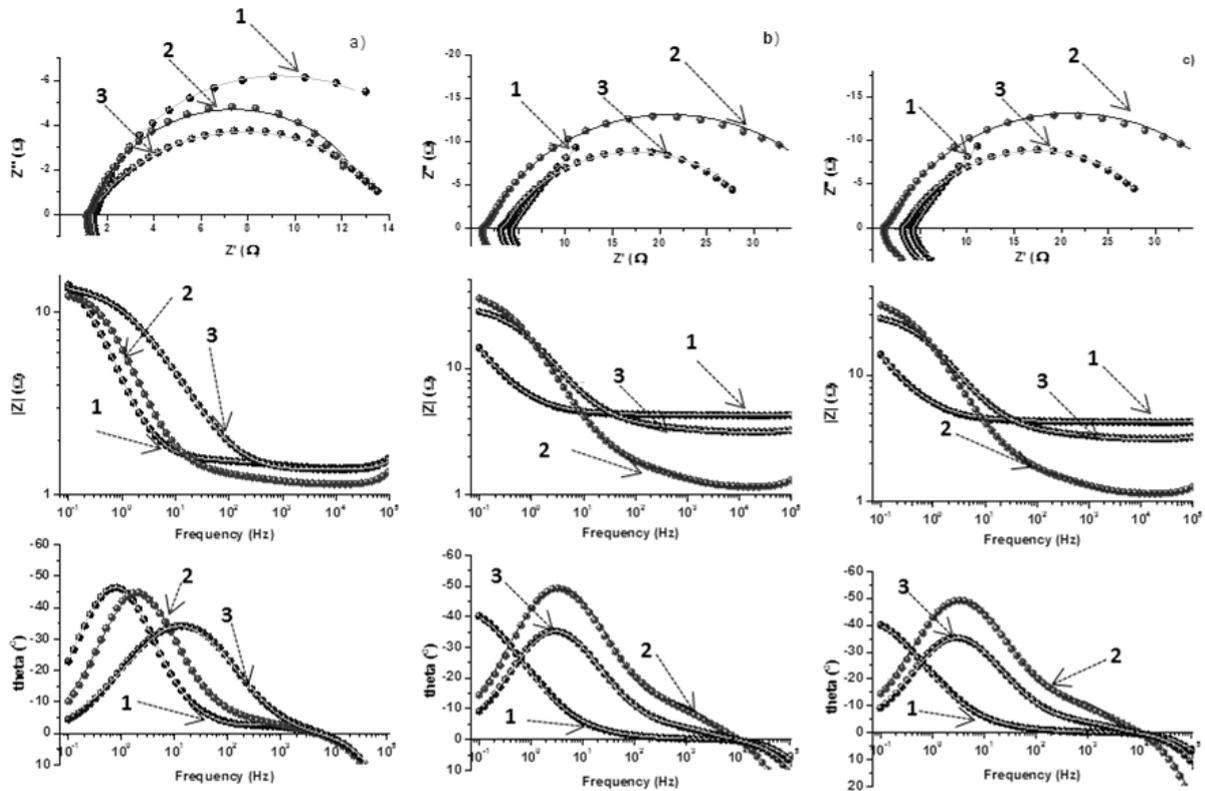


Figure 4. Nyquist and Bode plots of different electrodes and techniques: Zn+C (a), ZnO+C+2212 (b) and ZnO+C+2202 (c); 1- mechanical treatment, 2 – ball meal treatment, 3- ultrasound treatment.

Table 2. Calculated impedance parameters.

Sample	C1 [mF]	R1 [Ω]	CPE2 [mF.s ^{1-α]}	α	R2 [Ω]
1 (ZnO, MT)	1.87	0.14	0.054	0.851	15.62
2 (ZnO, BM)	1.79	0.189	0.0298	0.825	12.19
3 (ZnO, US)	1.20	0.601	0.015	0.706	12.08
4 (2201, MT)	1.8	0.35	0.096	0.89	11.2
5 (2201, BM)	0.348	0.51353	0.0107	0.748	42.67
6 (2201, US)	0.68	0.558	0.0139	0.689	22.72
7 (2212, MT)	0.648	0.029	0.108	0.68	86.77
8 (2212, BM)	0.387	0.520	0.012	0.745	39.08
9 (2212, US)	0.372	0.425	0.012	0.701	28.04

In Figure 4 are compared Nyquist and Bode plots of different electrodes and techniques and results from fitting procedure are summarized in Table 2.

It can be seen that the treatments do not have an unambiguous effect on the resistance R2, but they

definitely shift the processes to higher frequencies and therefore to lower time constants.

Relatively low frequencies and high capacitance correspond to surface phenomena. The electrode impedance is substantial and dominated by charge

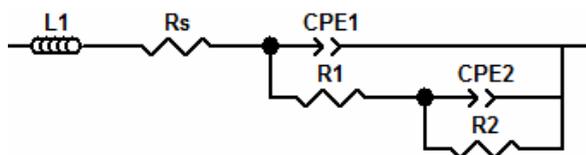


Figure 5. Equivalent circuit model for ZnO electrodes.

transfer, which is in agreement with our previous research [16].

The results from EIS measurements show that the method applied for homogenizing the ceramic with the zinc active mass, as well as its composition affect the electrode resistance, i.e. on the ongoing processes. In the presence of B(Pb)SCO 2201 the mixing in a ball-mill and ultrasound increases the resistance of the electrode and this effect is stronger with ball-mill treatment. This result shows that reducing the sonication time from 3 to 1 hour is not appropriate for obtaining a homogeneous active mass between zinc oxide particles and those of B(Pb)SCO 2201 ceramic [10].

Conversely, in the presence of B(Pb)SCCO 2212 the resistance decreases and the most significant decrease is achieved by sonication. The explanation of these results could be associated with the mechanism of ultrasound treatment. During the cavitation phase of the micro-bubbles micro fluid jets are generated that cause intensive mixing and homogenization. Local areas with very high temperatures and pressures are formed, which cause additional effects.

CONCLUSIONS

The present study investigates the influence of the different preparation methods on the mechanism of action of the active Zn mass with B(Pb)SCCO conductive cuprate ceramics as additives. The three different methods of preparation that were used are ball-milling treatment, ultrasound and mechanical (by hand) mixing. All methods were applied for 1/2 hour. The results show that the method of grinding in a ball-mill does not contribute to better homogenization of the ceramic additives in the active zinc mass. The ultrasound treatment for 1/2 hour leads to better homogenization of the active mass with B(Pb)SCCO 2212 and B(Pb)SCO 2201 ceramic and respectively the reduction of the electrode

resistance. The reason for the observed results can be explained on one hand by the processes that take place during ultrasonic treatment and on the other hand by the presence of calcium carbonate in B(Pb)SCCO 2212, which probably favours faster processes at the micro level. In the absence of B(Pb)SCCO 2212 more time is needed for the manifestation of the desired effect.

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CONFLICT OF INTEREST STATEMENT

The authors have no conflicts of interest to declare.

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