Study of Zn electrode active mass with added cuprates ceramic by electrochemical impedance spectroscopy

THE 11th BPU CONGRESS, 28.08-01.09.2022

Angelina Stoyanova-Ivanova [1], Ognyan Petkov [1*], Elefteria Lefterova[2], Yordan Marinov[1], Galia Ivanova [2], Georgi Hadjichristov[1] and Antonia Stoyanova[2]

[1] *Institute of Solid State Physics "Acad. Georgi Nadjakov" , Bulgarian Academy of Sciences*

[2]*Institute of Electrochemistry and Energy Systems "Acad. Evgeni Budevski", Bulgarian Academy of Sciences*

*Corresponding author: ogikrpetkov@issp.bas.bg

Financial support from the National Science Fund - Bulgaria is acknowledged. (Grant KP-06-N58-6/ 2021)

Abstract

The nickel-zinc electrochemical system is a promising candidate for alkaline batteries due to its low toxicity, high energy densities and power. Their main disadvantage is the solubility of the zinc electrode and the formation of dendrites during operation. Previous studies having used B(Pb)SCCO ceramic as additive in the Zn electrode mass proved its positive effect on improving the electrochemical properties[1,2]. Recently, the silver (Ag) is emerging as a promising component for the development of high-performance anodic materials for Zn-nickel batteries[3]. In the present work the effect of Ag additives, as well as conductive ceramics B(Pb)SCCO on the electrical properties and behavior of the Zn electrode was studied. The incorporation of these additives in the Zn electrode active mass was assisted by ultrasonic treatment. The phase composition and morphology of the electrode material were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). Zn electrodes prepared by inserting a Zn paste with a different amount of additive B(Pb)SCCO 2212 and Ag into the copper foam matrix were used as working electrode. The electrochemical behavior of the modified Zn electrodes was investigated using a three-electrode configuration in a 7M KOH electrolyte. The effect of the additives on the AC electrical response of the studied electrochemical system was estimated by electrochemical impedance spectroscopy (EIS).

References:

1. M. Mladenov et al., Electrode mass for zinc electrode of alkaline rechargeable batteries, BG Patent Reg. No 66730/28.08.2018
2. A. K. Stoyanova-Ivanova et al., Comptes rendus de l'Acad´emie bulgare des Sciences,75, No 3, 2022, pp.358-366
3. Y. Rong, Z. Yang, L. Deng, Z. Fu, Ceramics International 46 (2020) 16908

Materials and Methods

Bi_2O_3, PbO, CuO, $SrCO_3$ and $CaCO_3$ for B(Pb)SCCO 2212

↓

Mixing by agate ball mill for 1.30h

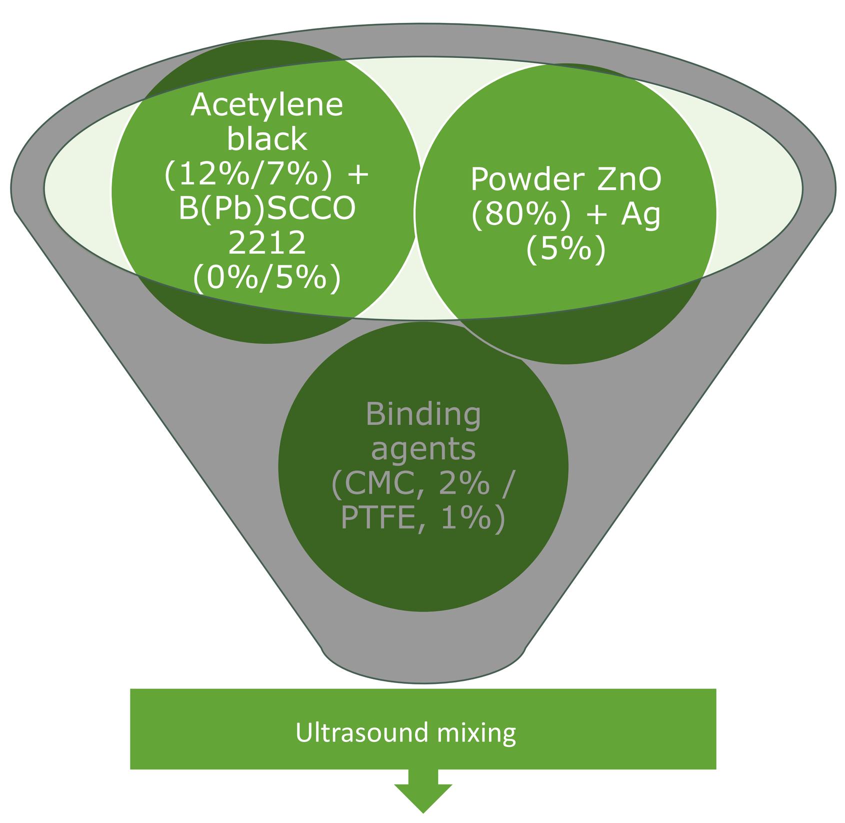
↓

Pressed into pellets at 5-6 MPa

↓

Heat treatment

First synthesis - 780 °C for 24h
Second synthesis - 830 °C for 48h

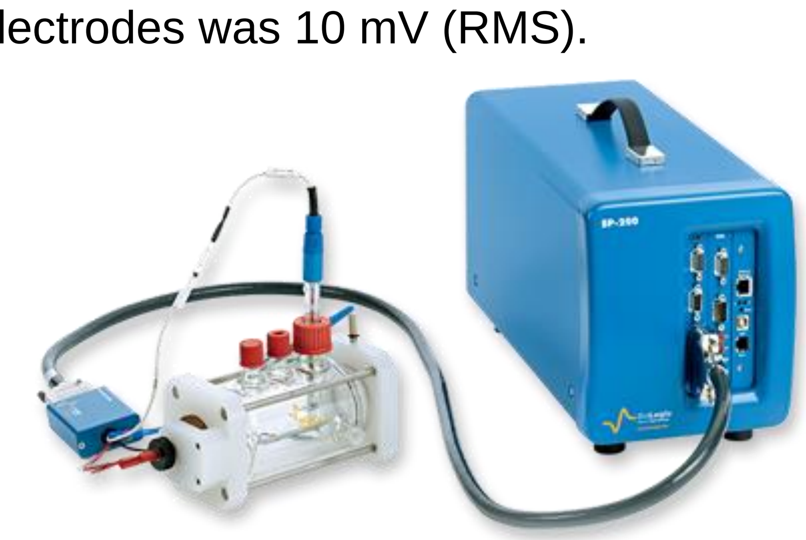


Insertion of the zinc paste in copper foam matrix

The microstructure of the electrode was studied by means of Zeiss EVO MA-15 scanning electron microscope (SEM) with LaB_6 cathode on the polished cross-section of the samples.

A Philips X-ray diffractometer PW 1030 having a θ-2θ Bragg-Brentano geometry, with Cu Kα radiation (30 kV, 20 mA) with a wavelength λ = 1.5406 Å and a scintillation detector was used to determine the crystallite sizes.

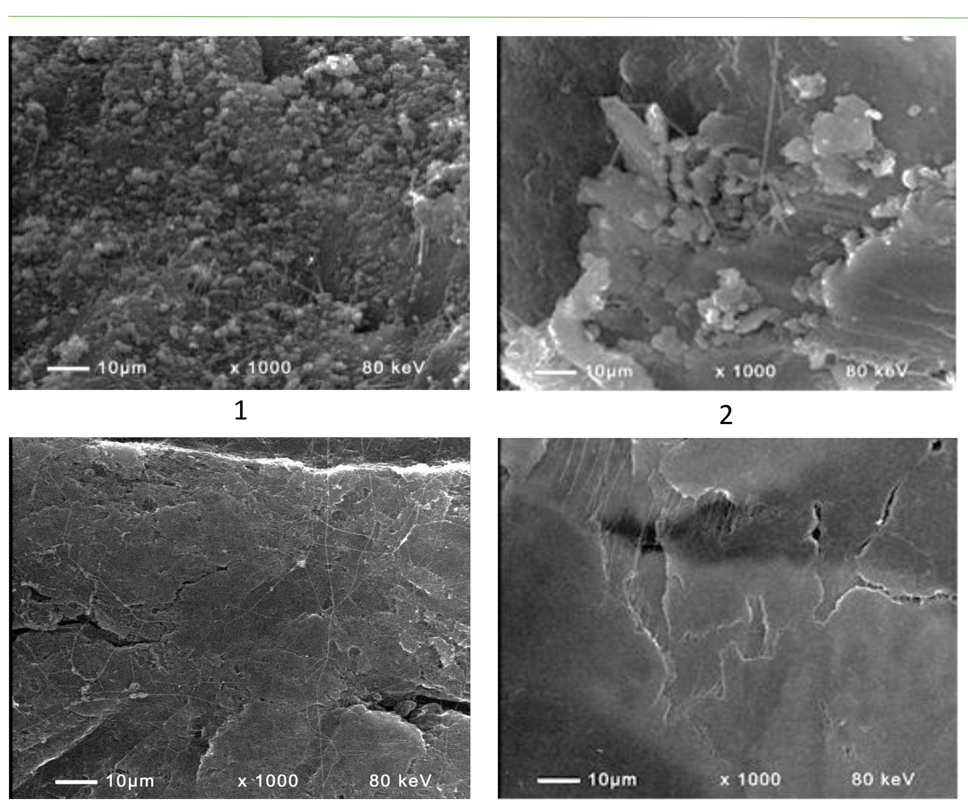
EIS measurement data were acquired using an impedance-meter BioLogic SP–200 in a three-electrode configuration. The electrical response of the ceramic modified electrode in 7M KOH electrolyte was registered in the 1 Hz – 1 MHz frequency range. EIS measurements were performed by a sine-wave signal perturbation. The amplitude of the AC voltage applied on the electrodes was 10 mV (RMS).



Bio-logic SP-200 potentiostat/galvanostat & three-electrode configuration experimental setup

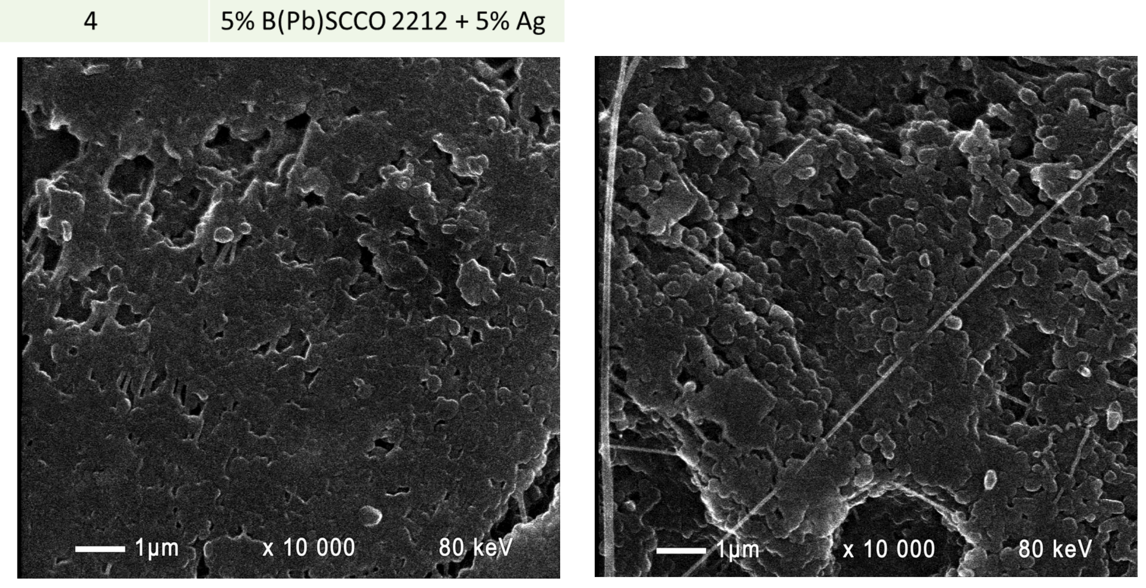
Results

SEM



1 2 3 4

Number of SEM	Composition
1	No additives
2	5% B(Pb)SCCO 2212
3	5% Ag
4	5% B(Pb)SCCO 2212 + 5% Ag
5	5% Ag
6	5% B(Pb)SCCO 2212 + 5% Ag



5 6

The SEM micrographs of the active mass display a formation of relatively homogenous surface with fine-grained structure. It is well seen the formation of a typical polycrystalline structure in the sample. The grains are relatively large (5-10 μm) without specific shape. Introduction of silver into the zinc active mass leads to smoothing of the electrode surface, which favors the performance of electrochemical processes. The morphology of the sample with 5% silver and 5% ceramics is rougher and in layers as seen in the micrographs. The formation of cracks is also observed, which are most likely the reason for the increase on the electrode resistance. Through XRD the crystallite sizes of ZnO, the ceramic and silver were calculated.

Crystallite size [nm]
- ZnO ≥ 70
- BSCCO 2212 ≥ 48
- Ag ≥ 45

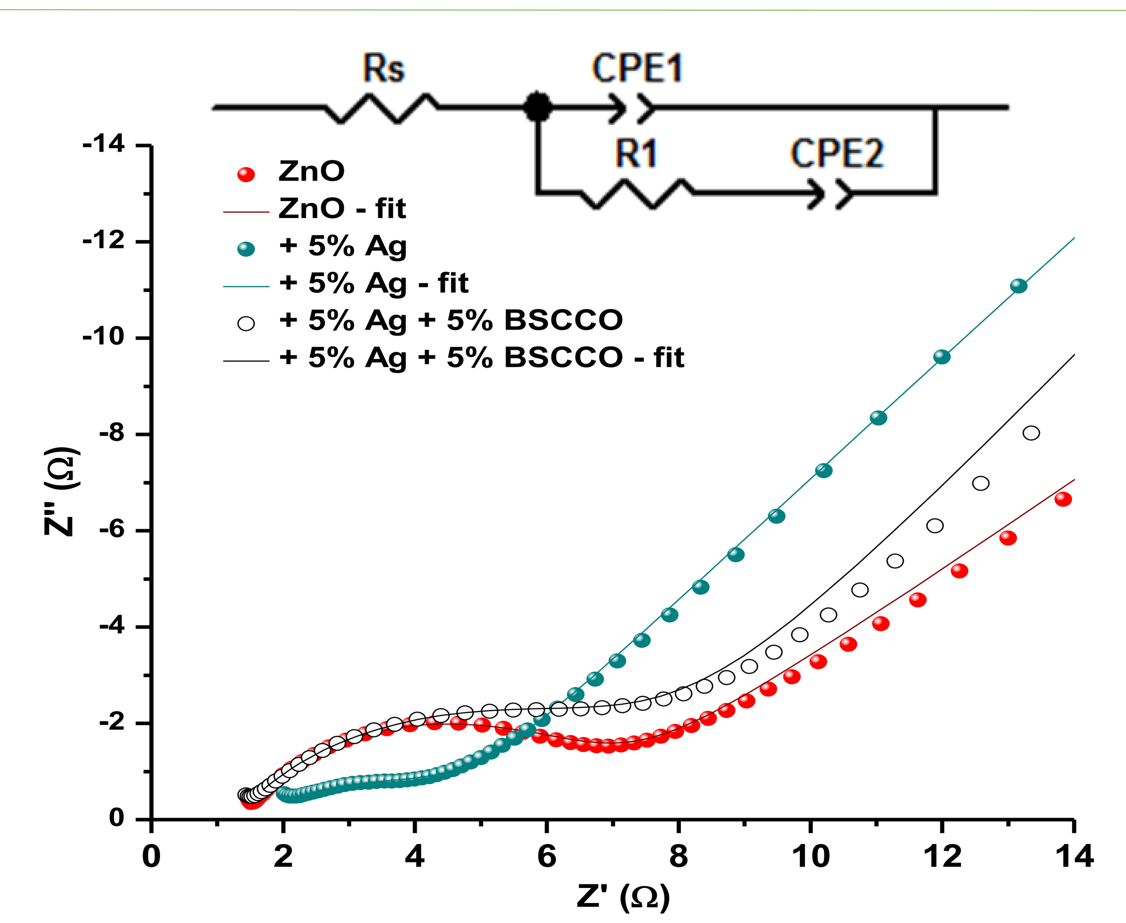
Impedance measurements

❖The presence of Ag at concentration of 5 wt.% in the ZnO mass of the anode leads to enhancement of it's static (DC) electrical conductivity while the inclusion of ceramic shows opposite effect: an increasing of R_1, not compensated by silver.

❖For the neat ZnO electrode, the diffusion is the determining process (n_2≈0.5).

❖The addition of Ag and BSCCO ceramics leads to the appearance of pseudocapacitive behavior (n_2=0.6) in the electrode impedance.

❖The performance of Ag / B(Pb)SCCO 2212 dopped Zn electrodes appear perspective for applications in Ni-Zn batteries, or other electrochemical systems. Further, the electrical conductivity data obtained by the complex electrical impedance are useful for improvement of the electrode preparation, as well as for elucidation the effect of the Ag and B(Pb)SCCO 2212 dopants on the electric transport properties.



Electrode	Rs	R1	CPE1 [mFs^{n-1}]	n1	CPE2 [mFs^{n-1}]	n2
Without additives	1.43	5.35	1.10	0.77	104	0.48
5% Ag	1.39	4.25	11	0.42	50	0.60
5% Ag + 5% BSCCO	1.27	7.02	1.69	0.67	33	0.61

Conclusion

- The nickel-zinc battery is a cheap, safe and eco-friendly energy storage alternative.
- By additions to the zinc electrode active mass the solubility and conductivity of the electrode can be greatly improved
- The BSCCO ceramic doping with ultrasound mixing leads to better particle distribution, better stability of the capacity and extension of the life of the electrode
- The silver doping with ultrasound mixing leads to smoothing out the surface of the electrode and improves conductivity