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## ELECTROCHEMICAL IMPEDANCE STUDY OF BSCCO (2212) CUPRATE CERAMIC ADDITIVE TO THE ZINC ELECTRODE IN Ni-Zn BATTERIES

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**Abstract.** Conductive cuprate BSCCO (2212) ceramics, exhibiting superconductivity at low temperatures (80 – 100K) can find other applications as well, such as an additive in the zinc electrode of nickel-zinc batteries. Ni-Zn cells are a potential cheaper alternative to replace toxic nickel-cadmium batteries. The positive effect of cuprate ceramic additives has been previously demonstrated. The study, presented here is focused on the electrochemical characterization of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$  (BSCCO 2212) nanocomposite conductive ceramics as an additive to the zinc electrode at 25°C and 50°C in an alkaline electrolyte containing KOH and  $\text{Na}_3\text{PO}_4$ .

Three coin type electrodes (15mm in diameter) were investigated by Electrochemical Impedance Spectroscopy measurements by a Bio-logic SP-200 potentiostat in a wide frequency range ( $10^6$  - 0.1 Hz). The tests were performed in a three-electrode electrochemical cell with different negative electrodes – one with “classic” conductive carbon additive, another with BSCCO 2212 additive, and the third without any additives (only ZnO). The obtained impedance spectra are compared and equivalent circuit models are proposed.

*Keywords:* electrochemical impedance, HTSC ceramics, BSCCO.

## **Introduction**

Nickel-Zinc (Ni-Zn) batteries are one of the oldest but still promising electrochemical energy storage solutions for hybrid/electric vehicles and portable electrical/electronic devices. Commercially available Ni-Zn batteries exhibit moderate specific energy ( $55 - 85 \text{ Wh kg}^{-1}$ ), high power density ( $140 - 200 \text{ Wh kg}^{-1}$ ), high open circle potential (1.705V), and a nominal cell voltage of 1.6V which is greater than that of Ni-Cd and Ni-MH batteries - (Huang et al., 2008; Cheng et al., 2007). Furthermore, compared to readily available battery technologies such as Li-ion, Ni-Cd, and Ni-MH, Ni-Zn batteries provide a low-cost and environmentally friendly alternative with comparable if not better performance per unit weight.

However, NiZn technology has not reached its full potential due to a variety of issues that are well documented in literature (Jindra, 1997; 2000; Shukla et al., 2001). Among these issues are the shape change of zinc electrode with increasing charge/discharge cycle count, zinc electrode passivation, and dendritic zinc growth leading to short-circuiting of the battery. In discharge process, zinc is dissolved as zincate ion ( $\text{Zn(OH)}_4^{2-}$ ) in alkaline electrolyte before zinc oxide precipitates. Highly mobile zincate ions are concentrated near the bottom of the electrode and precipitate as zinc oxide when the solubility limit is reached. This process leads to thickness non-uniformity of deposited zinc on the electrode with increasing charge/discharge cycle count and, combined with the dendritic growth of zinc during charging, eventually causes short-circuiting of the battery.

Passivation is also considered as one of the serious issues for the deterioration of zinc batteries. This phenomenon occurs when the dissolution of zinc produces a situation in which the solubility limit of zincate is reached in electrolyte close to the surface of the zinc electrode, and a zinc oxide insulating layer is formed on the electrode surface.

As a result of these issues, short cycle life and/or poor electrochemical performance have limited large-scale implementation of Ni-Zn batteries (Yuan et al., 2005; 2006a; Ma et al., 2008). Some of these issues are directly or indirectly related to formation of soluble zincate ions in alkaline solution during battery operation. The solubility limit of zincate is determined by the temperature and pH of alkaline solution.

Many attempts have been made to minimize the solubility and movement of zinc oxidation products in alkaline solutions and to improve physical and chemical stability of zinc electrode with increasing charge/discharge cycle count. These attempts include using organic and inorganic additives to the zinc electrode and electrolyte, tailoring separator structure to minimize dendritic zinc growth (Kritzer & Cook, 2007; Philips & Zhao, 2010) and using different electrode geometries (Cai & Park, 1996; McBreen, 1975).

One of the effective ways to minimize the above mentioned problems is to use various oxide additives, such as  $\text{Ca(OH)}_2$  (Yuan et al., 2006b; Yang et al., 2007),  $\text{Bi}_2\text{O}_3$  (Yuan et al., 2011),  $\text{PbO}$  (Shivkumar et al., 1998),  $\text{TiO}_2$  (Lee et al., 2011) in zinc electrode. 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 (Luo et al., 2013; Huang et al., 2008; Zhang et al., 2008). The positive effect on capacity (up to 30%) and cycling stability of cuprate ceramic additives has been previously demonstrated (Stoyanov et al., 2015; Stoyanova-Ivanova et al., 2015; Raicheff et al., 2016).

The aim of the present paper is to investigate the possibility of application of superconductive cuprate BSCCO 2212 ceramics as a multifunctional conductive additive to the zinc electrode mass in rechargeable alkaline Ni-Zn batteries. Through impedance spectroscopy the conductivity of Zn electrodes with BSCCO 2212 ceramics additive, with „classic“ carbon additive and electrode without any additives (only ZnO) has been investigated to obtain initial qualitative data about their electrical characteristics and behavior exposed to different temperature conditions.

## **Materials and methods**

### *Additive preparation*

Ceramic tablets of nominal composition:  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$  (BSCCO 2212) are obtained through solid state reaction. Powder samples of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$  are produced by two-stage conventional solid-state synthesis from high-purity (99.99 %) oxides -  $\text{Bi}_2\text{O}_3$ ,  $\text{CuO}$ ,  $\text{SrCO}_3$  and  $\text{CaCO}_3$ . After thorough mixing and grinding and initial heat treatment at  $780^\circ\text{C}$  for 24 hours in air the powder received is ground and pressed into pellets (5-6 MPa).

### *Electrode preparation*

The coin-type zinc electrodes used in the present study are prepared applying the same technological procedure described in (Stoyanov et al., 2015).

The electrode mass is composed of powder ZnO (99.99% pure, commercial product), acetylene black and binding agents – polytetrafluorethylene and carboxymethylcellulose and thoroughly mixed with distilled water to form a mushy paste. A matrix of nickel foam is used for the 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.

For comparison, similar zinc electrodes with electrode mass composed by ZnO, acetylene black and the same binding agents, but containing a “classic” conductive carbon additive and superconducting ceramic powder BSCCO 2212 additives at a concentration of 7% wt.% were also fabricated, applying the same technological procedure.

#### *Potentiostatic electrochemical impedance spectroscopy*

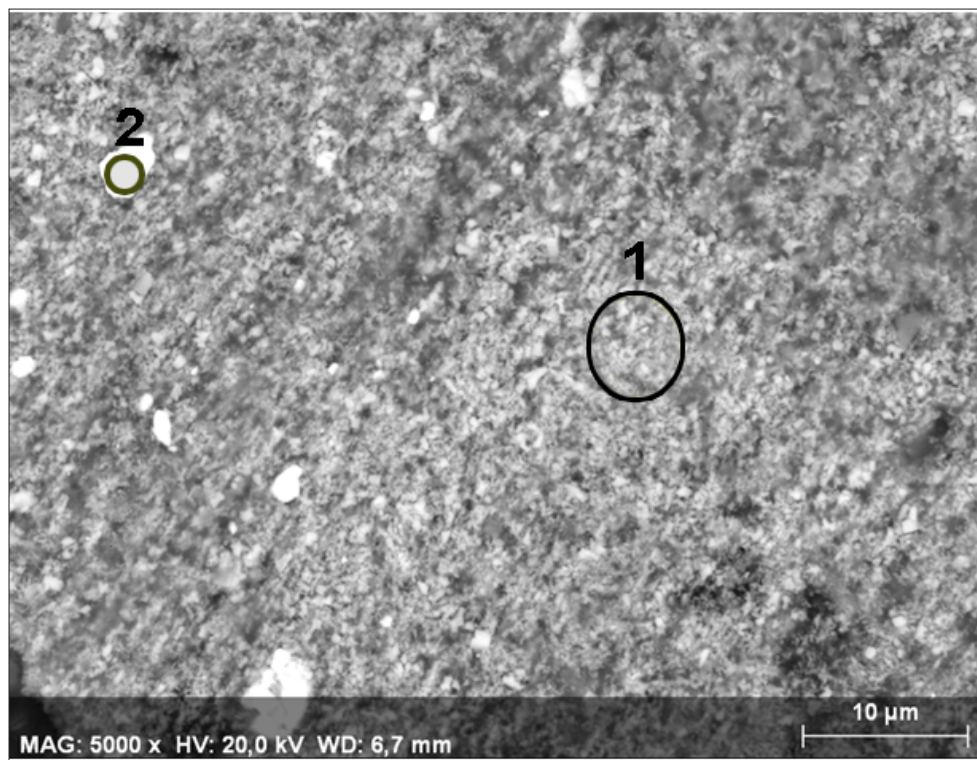
The electrochemical system SP-200: potentiostat/galvanostat was used to perform potentiostatic electrochemical impedance spectroscopy (PEIS) measurements. The obtained impedance spectra were fitted to an equivalent circuit model using the EC-Lab software. PEIS measurements were taken using the ZnO electrodes 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 potential is referenced to the open circuit potential of the working electrode. The applied sine-wave potential amplitude is 10mV, 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 1 MHz down to 0.1 Hz. The supporting electrolyte was alkaline electrolyte containing KOH and  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$  (Lilov et al., 2018). Impedance spectra were taken at 25°C and 50°C in order to examine electrical and electrochemical behavior at different temperature of Ni-Zn cells.

#### *Physicochemical characterization of electrode materials*

Surface morphology and elemental composition of the zinc electrode is studied by means of a Zeiss EVO MA-15 scanning electron microscope (SEM) with LaB6 cathode. The chemical composition is determined by X-ray microanalysis using energy dispersive spectroscopy (EDX) on an Oxford Instruments INCA Energy system. The qualitative and quantitative analyses are carried out at an accelerating voltage of 20 kV. The relative error of the analysis in determining the elemental composition percentage by weight is 0.5 to 1%.

### **Results and discussion**

The EDX spectra were taken in two regions (Fig. 1): on a part of the active electrode mass (Region 1; Table 1) and on a grain of BSCCO ceramic (Region 2; Table 2). Cuprate ceramics exhibit different reactivity towards water depending on pH. EDX verifies that the ceramic is not altered by the preparation process, most notably by the mixing of the paste with distilled water.



**Figure 1.** SEM image of analyzed electrode regions

**Table 1.** Elemental composition of active electrode mass

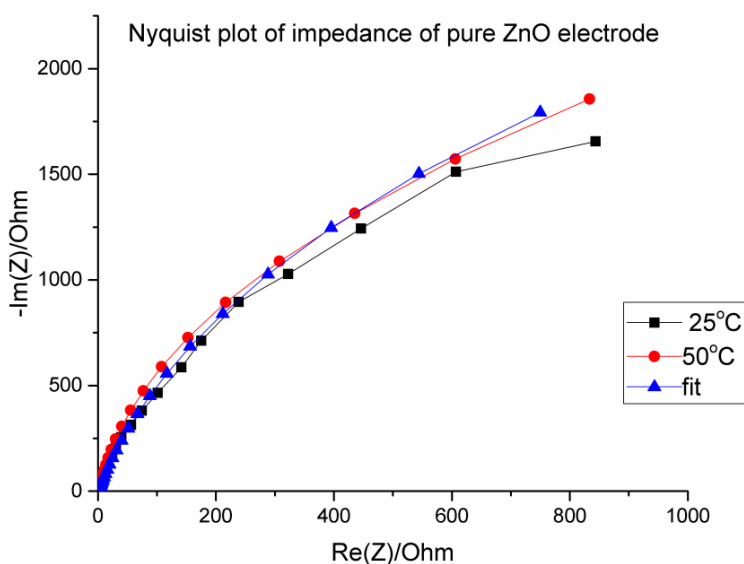
| Element  | Series   | unn.    | C norm. | C Atom. | C Error |
|----------|----------|---------|---------|---------|---------|
|          |          | [wt. %] | [wt. %] | [at. %] | [%]     |
| Zinc     | K-series | 49,72   | 65,12   | 33,25   | 1,4     |
| Oxygen   | K-series | 12,65   | 16,57   | 34,58   | 1,9     |
| Fluorine | K-series | 13,98   | 18,31   | 32,17   | 2,4     |
| Total:   |          | 76,35   | 100,00  | 100,00  |         |

Three coin type electrodes (15mm in diameter) – one with “classic” conductive carbon additive, another with BSCCO 2212 additive, and the third without any additives (only ZnO), were investigated in a wide frequency range ( $10^6$  - 0.1 Hz) in a three-electrode electrochemical cell.

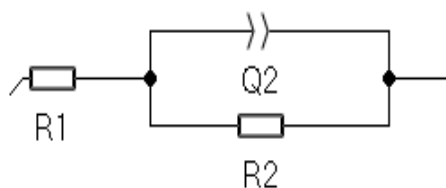
**Table 2.** Elemental composition of BSICO 2212 grain

| Element   | Series   | unn.   | C norm. | C Atom. | C Error |
|-----------|----------|--------|---------|---------|---------|
|           |          | [wt.%] | [wt.%]  | [at.%]  | [%]     |
| Bismuth   | M-series | 34,03  | 39,23   | 8,20    | 1,8     |
| Copper    | K-series | 9,58   | 11,05   | 7,59    | 0,3     |
| Calcium   | K-series | 4,10   | 4,73    | 5,15    | 0,2     |
| Strontium | L-series | 12,76  | 14,71   | 7,33    | 0,7     |
| Oxygen    | K-series | 21,66  | 24,96   | 68,16   | 3,4     |
| Zinc      | K-series | 4,62   | 5,33    | 3,56    | 0,2     |
| Total:    |          | 86,75  | 100,00  | 100,00  |         |

Electrochemical impedance spectra were taken at room temperature (25°C) and at 50°C in order to examine electrode kinetics near working conditions and at elevated temperatures. The Nyquist impedance plots for the ZnO electrode with no conductive additives is presented in Fig. 2. The electrode's impedance is substantial and dominated by charge transfer. The electrode's equivalent circuit model is presented in Fig 3.

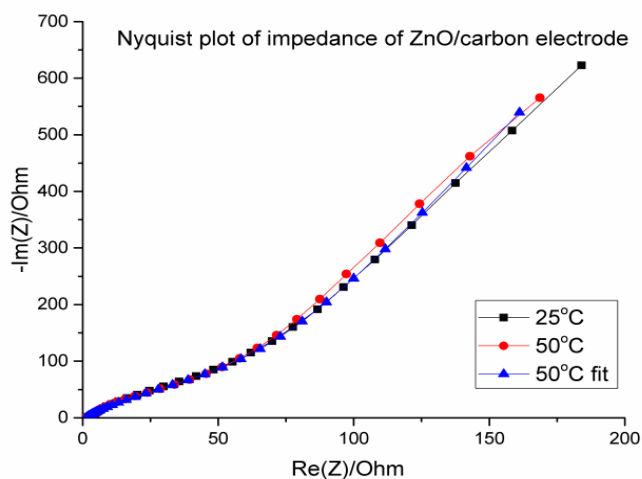


**Figure 2.** Nyquist plot of impedance of pure ZnO electrode at 25°C, 50°C and fit at 50°C

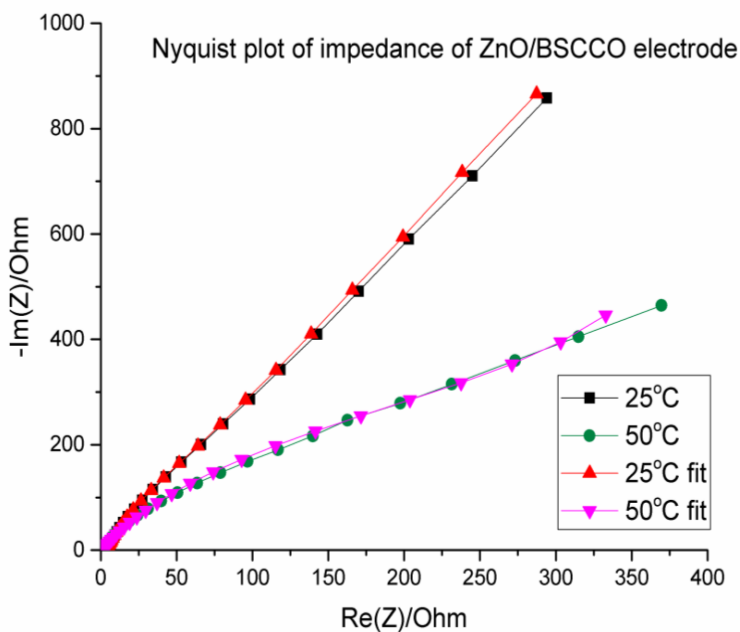


**Figure 3.** Equivalent circuit model for pure ZnO electrode

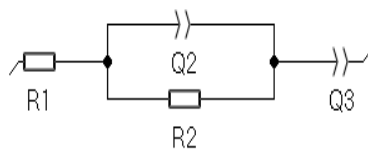
The impedance plots for the electrodes with carbon and BSCCO additives are presented in Figs. 4 and 5, respectively. In both cases the impedance is lowered. Their equivalent circuit model is presented in Fig. 6.



**Figure 4.** Nyquist plot of impedance of ZnO/Carbon electrode at 25°C, 50°C and fit at 50°C



**Figure 5.** Nyquist plot of impedance of ZnO/BSCCO electrode at 25°C, 50°C and fit at 25°C, 50°C

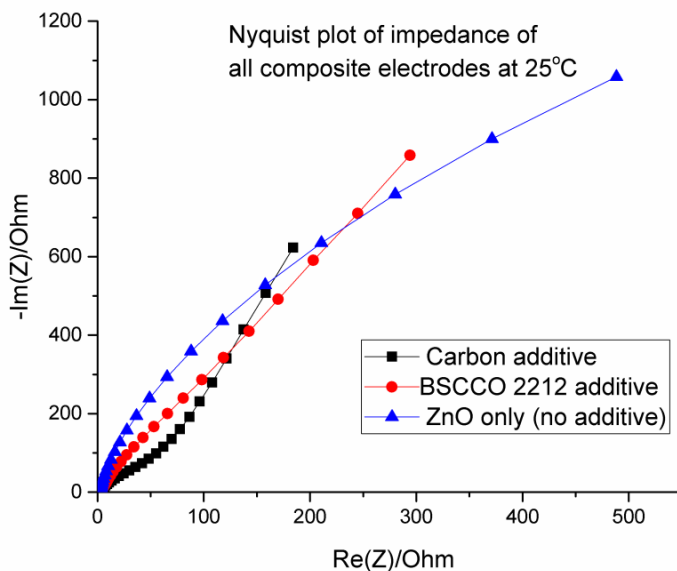


**Figure 6.** Equivalent circuit model for pure ZnO/carbon and ZnO/BSCCO electrodes

A change towards a diffusion limited process is observed. The electrode with a carbon additive displays minimal to no change in impedance with temperature. At 25°C the electrode with BSCCO displays mixed reaction control with a shift towards a purely diffusion limited process at the higher temperature (50°C).

The responses of all electrodes at 25°C are compared in Fig. 7. Although the real part of the complex impedance is substantially reduced compared to the electrode with no additives, the effect of BSCCO additives is not as pronounced as that of the

carbon additive. Further studies will be required to fully explain the positive effect of BSCCO ceramics on cycling stability.



**Figure 7.** Nyquist plot of impedance of all electrodes at 25°C

### Conclusion

Three coin type ZnO electrodes containing different conductive additives (carbon and BSCCO 2212) were physicochemically and electrochemically characterized. A ZnO electrode with no conductive additives is used as a baseline for comparison. EDX verifies that the ceramic is not altered by the preparation process. BSCCO 2212 ceramic additives successfully improve electrode conductivity. The effect is comparable to that of a conventional carbon additive, but electrodes with BSCCO exhibit much greater temperature dependence than the electrodes with carbon additives.

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