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Electrochemical impedance study of HTSC ceramics YBCO and BSCCO in presence of electrolyte

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Electrochemical studies of high temperature superconductuctors (HTSC) began immediately after their discovery and numerous studies of ionic transport in HTSC solid electrolytes were conducted. The search for approaches to the problems in HTSCs was largely based on analogies with electrochemical studies of semiconductors, since the majority of HTSC materials exhibit semiconducting properties at ambient temperatures. The analogy thus stimulated the electrochemical studies on the degradation of HTSC in water and acid solutions and their relative stability in strong alkaline solutions. HTSC cuprate ceramics find applications also as an additive in the zinc electrode in nickel-zinc batteries. Such cells are a potentially cheaper and easier to recycle, replacement for toxic nickel-cadmium batteries. Electrochemical tests showed that the Ni-Zn battery cells with YBCO and BSCCO superconducting ceramic additives in the zinc electrode exhibited good cyclic operation ability and capacity stability, as well as a higher specific capacity than the cells with a zinc electrode with a "classic" carbon conducting additive. The study presented here is focused on the electrochemical characterization of nanocomposite conductive cuprate ceramics - $Bi_2Sr_2CaCu_2O_x$ (BSCCO -2212), Bi_2Sr_2CuOy (BSCO - 2201) and $YBa_2Cu_3O_x$ (YBCO - 123) in the following electrolytes: 7M KOH, the electrolyte used in Ni-Zn cells, an alkaline phosphate (AF) - electrolyte containing KOH and $Na_3PO_4.12H_2O$, and a proprietary PSPAA electrolyte. The electrical conductivity of ceramic/electrolyte system was investigated by Electrochemical Impedance Spectroscopy measurements performed by a Bio-logic SP-200 potentiostat. The impedance responses for all ceramics are compared and discussed in terms of equivalent circuits.

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

INTRODUCTION

The expression "high-temperature superconductivity" HTSC has been used for several decades [l], but it changed from an abstract term to a real one only in 1986 after the famous publication of Bednorz and Muller [2]. All the more revolutionary, both in the fundamental and in the applied aspects, became the subsequent discovery of the oxide HTSC of the YBCO system with a T_c, higher than liquid nitrogen temperature, followed by the discovery of other cuprate systems with even higher characteristic values, such as BSCCO. Most HTSC oxides have the structure of perovskite (though some of them have a spinel-type structure), which pertains to more than 35 structural classes [3], and includes more than a hundred typical unit cells [4]. For fundamental studies of superconductivity in oxides, both the absolute T_c, values and the variety of properties and structures are essential.

Electrochemical studies of HTSC began immediately after their discovery and the numerous studies of ionic transport in HTSC solid electrolytes were conducted. Hence, the electrochemistry of HTSC can be considered as a direction in electrochemical science and technology [1].

The search for approaches to the problems in HTSCs was largely based on analogies with electrochemical studies of semiconductors [5-9], since the majority of HTSC materials exhibit semiconducting properties at ambient temperatures. Moreover, technological problems arising in the practical application of materials of these classes (such as in the electronics field) are similar. The analogy thus stimulated the electrochemical studies on the degradation of HTSC in water and acid solutions [10, 11] and their relative stability in strong alkaline solutions [1].

HTSC cuprate ceramics, exhibiting superconductivity at low temperatures (80-100K) find other applications as well, such as an additive in the zinc electrode in nickel-zinc batteries [11, 12], which might replace toxic nickel-cadmium batteries. The positive effect on capacity and cycling stability of cuprate ceramic additives has been previously demonstrated [12, 13]. Studies have revealed that YBCO samples are remarkably stable, thus leaving

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the superconducting properties of the 123-type phase unchanged after the alkaline treatment. The possibility of using the superconducting YBCO ceramics as a conducting additive to the zinc electrode mass of nickel-zinc alkaline rechargeable batteries was also studied. The electrochemical tests showed that the battery cells with a YBCO superconducting ceramic additive in the zinc electrode exhibited a better cyclic operation ability and capacity retention after prolonged cycling, as well as a higher (by about 30%) specific capacity than the cells with a zinc electrode with a "classic" carbon conducting additive to the zinc electrode mass and thus may contribute to extending the battery life [12].

Powder superconductive cuprate ceramic BSCCO 2212 system is produced by solid-state synthesis and physicochemically characterized. The chemical stability of BSCCO ceramics in alkaline medium of the Ni-Zn battery is confirmed by structural and morphological analysis (XRD, SEM and EDX) and the superconducting properties of samples are evaluated before and after prolonged exposure to 7M KOH. The electrochemical tests are carried out by Stoyanov et. al. [12] with conventional sintered type nickel electrodes and pasted zinc electrode with active electrode mass based on ZnO with addition of BSCCO powder or carbon (acetylene black) as conductive additives show that the zinc electrode with BSCCO ceramic additive exhibits very good cyclability, remarkable capacity stability and much higher discharge capacity at prolonged charge/discharge cycling in comparison to the zinc electrode with the "classic" carbon conductive additive. It is suggested that the addition of BSCCO ceramics improves not only conductivity and electrochemical homogeneity of the electrode mass and reduces the gas evolution but also stabilizes its porosity structure. The results obtained prove the possibility of application of superconducting BSCCO ceramics as a multifunctional additive to the active mass of the zinc electrodes for alkaline nickel-zinc battery systems [12].

In this work we examine the conductivity of YBCO and BSCCO HTSC ceramics through impedance spectroscopy to obtain initial qualitative data about their electrical characteristics and behavior exposed to different electrolyte solutions.

EXPERIMENTAL

Through solid state reaction ceramic tablets of nominal composition: $Bi_2Sr_2CaCu_2O_y$ (BSCCO 2212) and $Bi_2Sr_2CuO_y$ (BSCO 2201) were obtained. Powder samples of $Bi_2Sr_2CaCu_2O_y$ are produced by two-stage conventional solid-state synthesis from high-purity (99,99 %) reagents - Bi_2O_3, CuO, $SrCO_3$ and $CaCO_3$. After thorough mixing and grinding and initial heat treatment at 780°C for 24 hours in air the powder obtained is ground and pressed into pellets (5-6 MPa). BSCO 2201 was sintered at 830°C for 24 hours, BSCCO 2212 at 830°C for 48 hours in air atmosphere.

Another sample of nominal composition: $YBa_2Cu_3O_x$ (YBCO) was obtained. Powder samples are produced by solid-state synthesis from high-purity (99,99 %) oxides - Y_2O_3, CuO and $BaCO_3$. After thorough mixing and grinding the first stage is a heat treatment at 900°C for 21 hours. After grinding, the powder was sintered for a second time at 940°C under the same conditions, followed by a slow cooling and an additional annealing at 450°C for 2 hours. The pellets were then pressed at 5-6 Mpa and sintered for a third time at 950°C for 23 hours, and subsequently annealed at 450°C for 23 hours.

The electrochemical system SP-200: potentiostat/galvanostat was used to perform potentiostatic electrochemical impedance spectroscopy (PEIS) measurements applying the EC-Lab software. The impedance of the conductive ceramic tablets (YBCO and BSCCO) was measured using a two probe method. The samples are prepared with a rectangular shape and their surface area was calculated. Silver conductive paste was applied on two parallel and opposite faces, with known surface area and distance between them. The specific electrical resistance ρ was calculated taking the resistance value measured at the low frequency point of the impedance curve intersection with the real axis. PEIS measurements were also taken using BSCCO and YBCO as the working electrode (WE) a three electrode electrochemical cell. The working surface area of the electrodes was 0.4679 cm^2, 0.88 cm^2 and 0.257 cm^2 for BSCO 2201, BSCCO 2212 and YBCO, respectively. The counter-electrode (CE) was a platinum plate. The potential was measured relative to a saturated calomel electrode (RE). The applied potential is referenced to the open circuit potential of the working electrode. 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 noise free data. In all experiments the frequency was swept form 1 MHz down to 0.1 Hz. Three supporting electrolytes were used: 7M KOH, the electrolyte used in Ni-Zn cells, an alkaline phosphate (AF) electrolyte containing KOH and $Na_3PO_4.12H_2O$ [14], and a proprietary PSPAA electrolyte containing anti-corrosion agents. Impedance spectra were taken at room temperature in order to examine electrical and electrochemical behavior near the working conditions of Ni-Zn cells.

RESULTS AND DISCUSSIONS

The impedance of the BSCCO conductive ceramic tablets was measured using a two probe method. Fig. 1 shows the Nyquist plot of impedance of bulk BSCCO ceramics. From the real part of the impedance at the lowest frequency specific electrical resistance ρ was calculated to be 0.124 Ω.cm for BSCO 2201 and 5052.3 Ω.cm for BSCCO 2212. PEIS measurements were taken using BSCCO and YBCO as the working electrode (WE) in a three electrode electrochemical cell. The impedance spectra of BSCO 2201 and 2212 in the three different electrolytes are presented in Fig. 2, 3 and 4 for KOH, AF and PSPAA respectively.

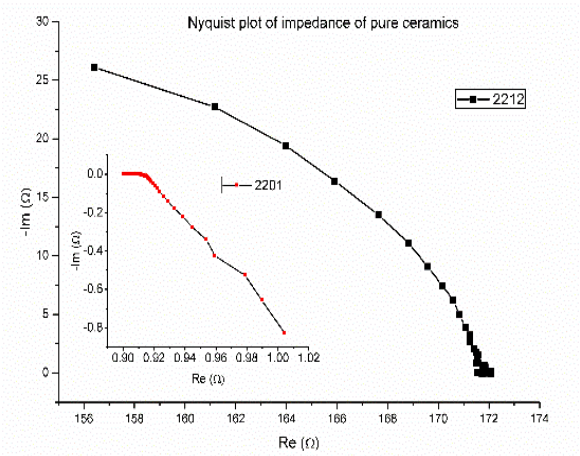

Fig. 1. Nyquist plot of the impedance for the pure ceramics.

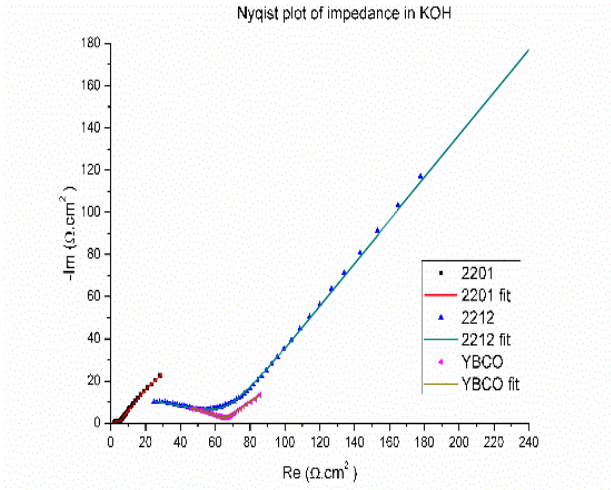

Fig. 2. Nyquist plot of the impedance for the ceramics in KOH electrolyte.

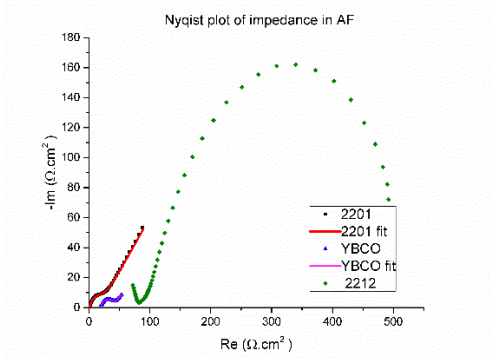

Fig. 3. Nyquist plot of the impedance for the ceramics in AF electrolyte

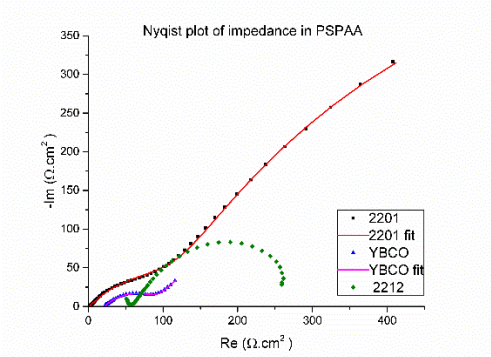

Fig. 4. Nyquist plot of the impedance for the ceramics in PSPAA electrolyte.

The raw data was normalized per unit surface area. Using the EC-Lab software we fitted the obtained curves to an equivalent circuit electrode model presented in Fig. 5a for BSCCO 2212 and YBCO and Fig 5b for BSCO 2201. Figures 2, 3 and 4 show the curves of the fits related to the obtained measurement data. The reasoning behind these models is supposition of surface modification observed in BSCCO ceramics on exposure to electrolyte [12].

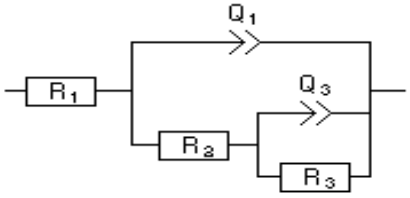

Fig. 5a. Proposed equivalent circuit model for BSCCO 2212 and YBCO ceramics.

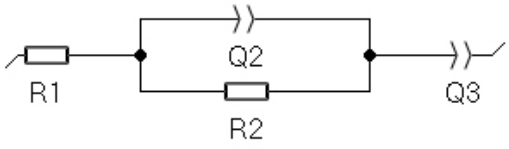

Fig. 5b. Proposed equivalent circuit model for BSCO 2201 in AF.

Table 1. Area-normalized parameter values obtained by curve-fitting

	BSCO 2201			BSCCO 2212	YBCO			(Units)
Model Param.	Electrolytes							
	KOH	AF	PSPAA	KOH	KOH	AF	PSPAA	
R1	1.70031	0.66838	1.75573	-171.952	8.468	18.200	21.739	$\Omega.cm^2$
Q1	6.73E-04	-	5.54E-04	1.03E-04	1.87E-4	1.53E-03	1.32E-03	$F.s^{(a-1)}cm^{-2}$
a1	0.5728	-	0.5125	0.1523	0.3162	0.5031	0.4772	-
R2	3.80597	16.9092	178.345	251.944	58.8016	25.664	82.856	$\Omega.cm^2$
Q2	-	4.34E-04	-	-	-	-	-	$F.s^{(a-1)}cm^{-2}$
a2	-	0.7165	-	-	-	-	-	-
Q3	1.47E-02	1.34E-02	1.31E-03	2.86E-03	3.00E-03	5.03E-03	2.03E-03	$F.s^{(a-1)}cm^{-2}$
a3	0.5784	0.41	0.7162	0.5235	0.4467	0.4553	0.698	-
R3	180.928	-	1505.85	22242.88	135.284	85.915	209.789	$\Omega.cm^2$

Degradation products may be less conductive and it is likely that they create a porous layer blocking the electrode surface. Here R1 represents the electrolyte resistance between RE and WE, R2 is the polarization resistance, R3 is the resistance of the electrolyte confined in the pores. Q1 and Q3 are the outer surface and pore double layer capacitances. Capacitances are substituted with constant phase elements (CPE) due to surface inhomogeneity, roughness and varying degrees of surface modification. Equivalent circuit parameter values are presented in Table 1. In the case of BSCO 2201 in the alkaline phosphate electrolyte another circuit model was used, presented in Fig. 5b, where R1 and R2 have the same meaning, while Q2 is equivalent to Q1. However, the behavior of BSCCO 2212 in the PSPAA and alkaline phosphate electrolytes could not be modeled by these equivalent circuits. The real part of the impedance at the lowest frequency is presented further below.

The parameter "a" describes the variation of the constant phase elements' impedance from purely capacitive (a=1) to purely resistive (a=0).

It must be noted that for BSCCO 2212 in KOH R1 is extrapolated by the software to a negative value due to lack of information about higher frequency behavior. At the highest frequency of 1 MHz the real part of the complex impedance is measured to be 24.64 $\Omega.cm^2$. The real part of the impedance of BSCCO 2212 at the lowest frequency is 492.03 $\Omega.cm^2$ for the AF electrolyte and 258.89 $\Omega.cm^2$ for PSPAA (fig.3, fig. 4).

BSCO 2201 exhibits the lowest values for R2 in both KOH and AF, with R2 being lowest in KOH. In the case of YBCO the opposite is true – R2 is smaller in AF than in KOH. In PSPAA R2 is substantially higher for both BSCCO 2201 and YBCO. While both BSCCO ceramics impedance varies substantially depending on the electrolyte solution content, YBCO displays less variation. The PSPAA electrolyte has an effect of increasing the polarization resistance for BSCO 2201 and YBCO and decreasing it in BSCCO 2212.

CONCLUSIONS

In this work we examined the conductivity of BSCCO and YBCO conductive ceramics through impedance spectroscopy to obtain initial qualitative data about their electrochemical characteristics and behavior exposed to various electrolyte solutions as a basis for their potential application as a conductive additive in Ni-Zn batteries. An equivalent circuit model was proposed and cell parameters were obtained through curve fitting. BSCO 2201 and YBCO exhibit lower overall resistance, BSCO 2201 and BSCCO 2212's behavior strongly depends on electrolyte composition. Results suggest that among the three examined ceramics BSCO 2201 is the best candidate for a conductive additive for the zinc anode in Ni-Zn batteries.

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ЕЛЕКРОХИМИЧНИ ИМПЕДНАСНИ ИЗСЛЕДВАНИЯ НА ВИСОКО ТЕМПЕРАТУРНИ СВРЪХПРОВОДИМИ КЕРАМИКИ ОТ ВИДА YBCO И BSCCO В ПРИСЪСТВИЕ НА ЕЛЕКТРОЛИТИ

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(Резюме)

Електрохимичните изследвания на високотемпературни свръхпроводници (ВТСП) започват непосредствено след тяхното откриване, като от тогава са проведени многобройни изследвания върху йонния транспорт в тях, с цел приложението им за електроди. Подходите за изследване на ВТСП се базират основно на аналогии с електрохимичните изследвания на полупроводниците поради това, че повечето от тях проявяват полупроводникови свойства при стайна температура. Тази аналогия е стимулирала проучвания на тяхната деградация в кисели и неутрални водни среди и сравнителната им стабилност в силно алкални разтвори. В последно време ВТСП намират приложение и като добавка в състава на цинковия електрод в никел-цинкови батерии. Тези батерии са перспективен кандидат за замяна на токсичните никел-кадмиеви батерии. Електрохимични тестове показват, че Ni-Zn клетки с добавки от YBCO и BSCCO свръхпроводящи керамики в масата на цинковия електрод, показват повишен специфичен капацитет и по-голяма стабилност на капацитета, при голям брой цикли на зареждане и разреждане Настоящото изследване се фокусира върху електрохимичното характеризиране на нанокомпозитни проводящи купратни керамики от вида $Bi_2Sr_2CaCu_2O_x$ (BSCCO - 2212), $Bi_2Sr_2CuO_y$ (BSCO - 2201) и $YBa_2Cu_3O_x$(YBCO - 123) в следните електролитни разтвори: 7M KOH - електролит използван в Ni-Zn батериите, алкален фосфатен (AF) електролит - съдържащ KOH и $Na_3PO_4.12H_2O$ и специализиран PSPAA електролит. Проводимостта на системата керамика/електролит е изследвана чрез използване на електрохимична импедансна спектроскопия, проведени с потенциостатична система Bio-logic SP-200. Импедансните характеристики на керамиките в различните електролити са сравнени и обсъдени посредством предложени еквиваленти електрохимични схеми. Предложен е модел, описващ елементите на електричната верига и са получени стойностите на параметрите, посредством апроксимиране на спектралните криви. Измерените електрически съпротивления на купратните свръхпроводими керамики от вида BSCO 2201 и YBCO показват относително ниски стойности. Поведението на BSCO 2201 и BSCCO 2212 силно зависи от състава на електролита. Резултатите показват, че от трите изследвани керамики, BSCO 2201 е с най ниско съпротивление и е най-подходяща за проводима добавка към цинковия анод в никел-цинковите батерии.

Ключови думи: електрохимичен импеданс, HTSC керамики, BSCCO, YBCO