



Production of brown inorganic pigments with spinel structure using spent zinc-carbon batteries

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Abstract

In recent years, there has been an increase in the production of zinc-carbon batteries to fulfil the demand for portable energy. This has led to an increase in the spent batteries disposal, which can cause environmental problems. In this study, inorganic brown pigments were produced using electrode materials from spent zinc-carbon batteries with the aim of recycling this residue as it is toxic to the environment and human health when disposed incorrectly. The pigments were produced by the solid state reaction between the oxides mixtures from spent batteries and chromium oxide and heat treated at 1200 °C for two hours. The produced pigments were stable and showed good colour and opacity when applied to ceramic pieces at a decorative burning temperature (850 °C). At 1050 °C, only the ZMC100 sample (with initial composition having $\text{ZnMn}_2\text{O}_4 : \text{Cr}_2\text{O}_3$ molar ratio of 1 : 1) showed stability. A good result was obtained when the produced samples were compared with the standards produced by solid-state reaction of the pure commercial oxides. The compounds produced during battery discharge, favoured the formation of ZnMn_2O_4 with higher purity at low temperatures. Hence, the pigment produced using dry electrode materials as a precursor was more crystalline than the synthetic sample obtained under the same conditions.

Keywords: zinc-carbon, spent batteries, recycle, spinel structure, brown pigment

I. Introduction

In recent years, the consumption of portable batteries has been increased due to the presence of many advantages, such as low cost and possibility of application of range of devices such as radios, calculators, and cameras [1–4]. Brazil produces about 1.2 billion portable batteries per year, while China has an annual production of over 15 billion portable batteries [5]. Zinc-carbon (Zn-C) batteries, classified as primary batteries (non-rechargeable batteries), correspond to 70% of the Brazilian market [5,6]. This kind of battery is composed of a metallic zinc anode, manganese dioxide as the cathode, and ammonium or zinc chloride as the electrolyte

[1,6]. This battery also has a graphitic cylinder that acts as a current collector and retainer for moisture [1,6]. In many countries, Zn-C spent batteries are disposed of in landfill, or they are incinerated. However, leaching of toxic metals or emission of hazardous gases can contaminate the environment [6]. In addition, the storage capacity of landfills is also a problem that causes an increase in disposal costs [1]. Hence, recycling has been implemented in many countries, such as Brazil, USA, and the European Union [1,7].

Many papers have been published on treatments to recover ZnO and MnO₂ (separately) from spent Zn-C batteries. Deep *et al.* [8] reported recuperation of ZnO nanoparticles with good properties for application in sensors, biology, and solar cells, while the recovered MnO₂ was free of impurities, and it also presented good properties for many applications. Using fine con-

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control over particle size by adjusting gas flow rates, Ebin *et al.* [9] reported an interesting process for Zn recovery with a nano-range particle size. Recently, Roy *et al.* [10] reported graphene production from a Zn-C graphite electrode, suggesting an interesting way to recycle the carbon electrode and increase the range of applications for spent Zn-C batteries.

In this study, we report the application of electrode materials using spent Zn-C batteries as raw material for the production of brown inorganic pigments based on Zn-Mn-Cr oxides. This application was chosen as the electrode materials contain high amount of zinc and manganese and also because of their ability to form spinel-structure useful in many applications, such as pigments, catalyst, varistors, and semiconductors [11]. For the pigment industry, compounds with a spinel structure are well-known due to their thermal stability and intense colour [12,13]. The insertion of chromium to Zn-Mn spinel was chosen to produce a pigment with a composition comparable to brown commercial pigments, encoded DCMA 13-51-7, a spinel of manganese, zinc, and chromium oxides [14].

II. Experimental procedure

2.1. Pigment preparation

D-sized spent batteries, used in this work, were supplied by the company Kurashiki of Brazil (they are used batteries in flashlights). Spent zinc-carbon batteries were opened, and the electrode materials were manually removed, dried, and passed through 325 mesh sieve (aperture 45 μm), giving a sample labelled as DEP (dry electrode paste). The DEP sample was milled in a ball mill with distilled water for 4 h; The milling of DEP was carried out in a ball mill composed of a polypropylene (PP) bottle with a capacity of 250 ml (diameter 6 cm and length 13 cm) and cylindrical grinding elements (1 cm in diameter, 1 cm in height and weight of 3 g) of magnesia-stabilized zirconia. The sample weight used in each batch was 4 g plus 225 g of grinding elements and water up to 125 ml. The rotation of the milling flask was 120 rpm. This step was aimed to remove many of the

soluble compounds such as chlorides, potassium, ammonium ions among others and to decrease the size of the particles. Then, the slurry was filtered and dried in laboratory oven at 100 °C for 12 h. The composition of the milled DEP sample obtained by X-ray fluorescence (XRF) is shown in Table 1. The XRF analysis was performed in the form of loose powder in a Panalytical Epsilon 3 XLE equipment. The milled and dried DEP obtained was thermally treated at 800 °C for 2 h to produce the sample denoted ZM. This sample was used as a precursor for the production of pigments with different chromium oxide contents (Cr_2O_3 , Dinâmica, 99%), synthesized by solid-state reactions (Table 2). The ZM sample and different amounts of chromium oxide were milled in a ball mill with isopropyl alcohol for 24 h. The samples were milled and dried under conditions similar to those used for the DEP sample. Then they were dispersed through a 325 mesh sieve (aperture 45 μm). Finally, the samples were placed in a muffle furnace and fired in static atmospheric air. After cooling the samples were removed from the oven.

Two additional samples were synthesized from the pure raw materials to obtain standards for comparison. The first one, labelled ZMS, is a synthetic standard of the ZM samples produced under the same thermal conditions (800 °C, 10 °C/min) using the pure ZnO (Synth, 99%) and MnO (Sigma Aldrich, 99%). The used molar ratio of the oxides was 1 : 2, to obtain the desired phase ZnMn_2O_4 . The second one, labelled ZMCS, is a standard for the ZMC100 sample produced under the same thermal conditions (1200 °C, 10 °C/min) using Cr_2O_3 (Dinâmica, 99%) and ZMS in molar ratio of 1 : 1.

The samples were characterized by X-ray powder diffraction at the Brazilian Synchrotron Light Laboratory (LNLS, Campinas, Brazil) using synchrotron light in the XRD1 beamline with 12 keV energy ($\lambda = 1.03320 \text{ \AA}$) in the range of 10° to 80° with a step of 0.004° [15]. The samples were placed in 0.3 mm-diameter capillary tubes and measured five times to get the average diffractograms. Each analysis was performed for 10 min with 2 min for each repetition. For the total diffractograms, the intensity of the sample holder

Table 1. Chemical analysis in wt.% of DEP sample obtained by XRF

Mn	Zn	O	Fe	Cl	Al	Si	K	P	Ti	Ca	Ce	Others
54.85	17.41	16.87	4.36	2.16	1.54	1.15	0.64	0.29	0.18	0.15	0.13	< 0.25

Table 2. Syntheses conditions

Sample	Precursor	Molar ratio precursor* : Cr_2O_3	Thermal treatment conditions
ZM	DEP	1 : 0.00	800 °C, 10 °C/min, 2 h
ZMC25	ZM	1 : 0.25	1200 °C, 10 °C/min, 2 h
ZMC50	ZM	1 : 0.50	1200 °C, 10 °C/min, 2 h
ZMC75	ZM	1 : 0.75	1200 °C, 10 °C/min, 2 h
ZMC100	ZM	1 : 1.00	1200 °C, 10 °C/min, 2 h
ZMS	ZnO, MnO	1 : 0.00	800 °C, 10 °C/min, 2 h
ZMCS100	ZMS	1 : 1.00	1200 °C, 10 °C/min, 2 h

*To produce the pigments, it was assumed that sample ZM was only composed of ZnMn_2O_4

was discounted using equation 1:

$$I_s = I_t - I_c \frac{MC_s}{MC_c} \quad (1)$$

where I_s is the intensity of the sample without the specimen holder signal, I_t is the total intensity (sample and specimen holder), I_c is the intensity of the empty specimen holder, and MC_s and MC_c are experimental parameters of the calibration of the samples and the specimen holder, respectively.

Sample morphology was analysed by field-emission scanning electron microscopy (FE-SEM, TESCAN MIRA3 LM, at 15 kV) using carbon tape under the samples and a 3 nm thick layer of gold-palladium alloy.

2.2. Application of pigments

For application as ceramic pigments, two different transparent frits were used: i) F1 with SiO_2 , Al_2O_3 , and CaO (having high fusion temperature of 1050°C) and ii) F2 with SiO_2 and K_2O (having low fusion temperature of 850°C). Both were Pb-free and had low ZnO contents. To prepare enamel, the frit (95 wt.%) and the pigment (5 wt.%) were homogenized in a ball mill with isopropyl alcohol for 5 min. Alcohol was removed, 50 wt.% water was added, and the enamel was applied to the ceramics using a 0.5 mm thick Binil manual applicator. Ceramic pieces with enamel were thermally treated at 1050°C (frit F1) or 850°C (frit F2) at a rate of $10^\circ\text{C}/\text{min}$ and holding time of 20 min.

Polymer pigmentation was obtained using polymethylmethacrylate, PMMA (99 wt.%) and pigment (1 wt.%). After curing, the mixture was compressed uniaxially at 75 MPa for 2 min to produce cylindrical discs; this procedure was adapted from Vishnu *et al.* [16]. A standard was produced without pigment under the same conditions.

A commercial brown pigment (CBP) with a spinel structure which is composed of zinc, manganese, chromium, and iron was used as the commercial standard for the pigmentation tests.

The colour properties of the powder pigments, coloured ceramics and polymer were obtained by dif-

fuse reflectance spectroscopy in the ultraviolet-visible region (DRS UV-Vis, Varian CARY 50) in the wavelength range of 360–800 nm using a Barrelinio™ probe, illuminator D65, standard angle observer 10° , and standard white barium sulphate, BaSO_4 . The CIE $L^*a^*b^*$ colorimetric coordinates were obtained using Color (Varian) software.

III. Results and discussion

3.1. ZM samples

DEP is a very heterogeneous compound with many crystalline phases, such as ZnO , C , MnO_2 , Mn_3O_4 , Mn_2O_3 , and KCl [13,17]. The milling of DEP with water was performed for two reasons. The first reason was to remove any residual chloride ions (Cl^-) present as a result of using zinc or ammonium chloride as the electrolyte in the batteries and thus reducing the Cl^- content from about 15% to less than 2%. This procedure is very important because the Cl^- ion can be oxidized during the thermal treatment, emitting chlorine gas (Cl_2) that is dangerous to human health [18]. The second reason was to reduce the particle size to favour the diffusion of ions in the solid-state reaction, aiming to obtain the smallest possible amount of secondary phases. After the calcination of the DEP sample at 800°C for 2 h, it had a weight loss of 32%, which can be attributed to the presence of graphitic carbon used in the batteries to improve electrical performance. Figure 1 shows micrographs of the DEP sample, and the ZM sample produced after thermal treatment at 800°C without and with milling. Clearly, the ZM sample prepared with milling is more homogeneous, favouring application in the solid-state reaction.

Diffraction patterns of the samples ZM produced without and with milling are shown in Fig. 2. Two samples consist mainly of ZnMn_2O_4 crystalline phase with a spinel structure with tetragonal system and $I41/amd$ symmetry (JCPDF 24-1133). However, the sample without granulometric treatment has two peaks with a broad base indicating the presence of the residual Mn_3O_4 phase and proving the need for milling. Thus, the study of pigments was continued using only ZM produced

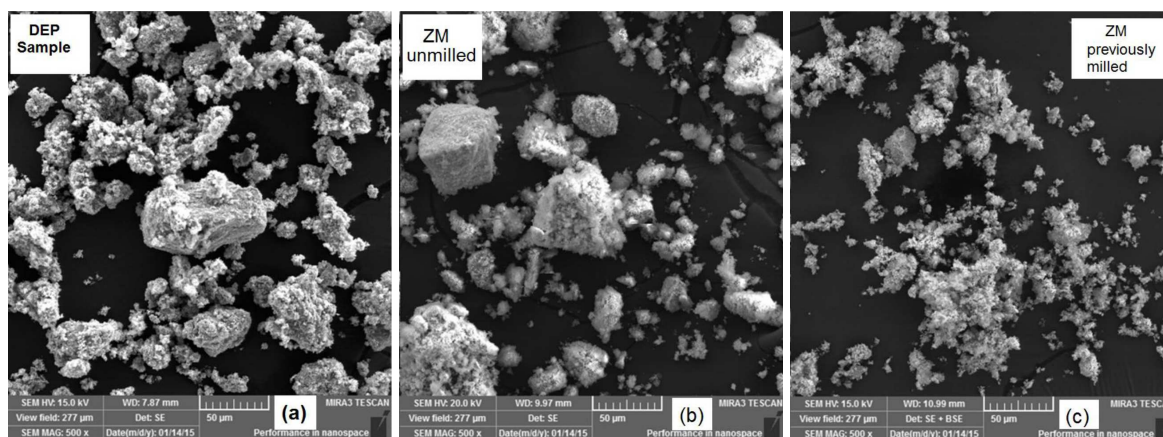


Figure 1. FE-SEM micrographs of the samples calcined at 800°C : a) DEP, b) unmilled ZM and c) milled ZM

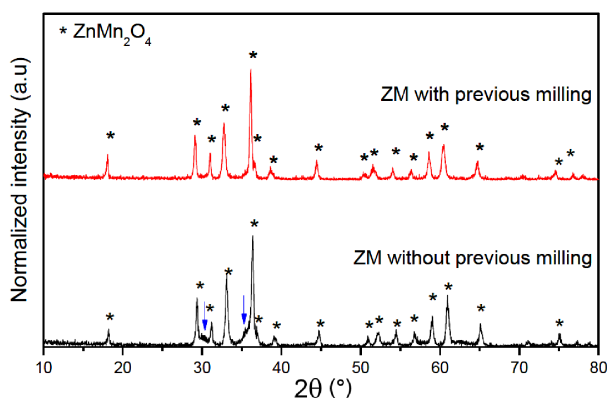
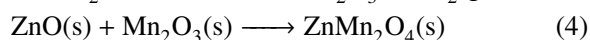
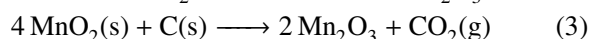
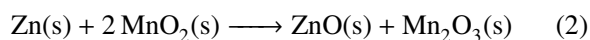


Figure 2. X-ray powder diffractograms of ZM produced without and with DEP sample milling (arrows indicate broad peaks due to an Mn_3O_4 secondary phase)

with milling. The formation of the ZnMn_2O_4 phase can be associated with several reactions: Eq. 2 shows the production of ZnO and Mn_2O_3 by the discharge of a Zn-C battery [1]; Eq. 3 shows the production of Mn_2O_3 from the redox reaction of C with MnO_2 ; Eq. 4 shows the reaction of ZnO and Mn_2O_3 , forming the ZnMn_2O_4 spinel identified by XRD analysis.



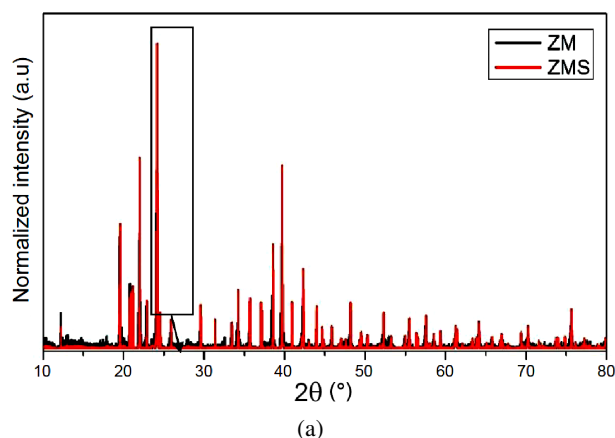
The observed formation of ZnMn_2O_4 from residue is very important, confirming it as a viable method for recycling electrode materials from spent Zn-C batteries, mainly, because it is now possible to produce a crystalline phase with good purity using a simple, reproducible, and cheap method. X-ray powder diffractogram of the standard ZMS sample (produced from ZnO and MnO under the same processing conditions) used for comparison is shown in Fig. 3. The presence of impurity ZnO phase can be observed. This suggests that the conditions were not adequate for this reaction as it was not possible to produce pure ZnMn_2O_4 phase.

These results suggest that spent batteries are interesting as a raw material because it is possible to produce high-purity and crystalline phases from them, at low temperatures; moreover, they are an interesting alternative, cheap, and rapid route for production of ZnMn_2O_4 .

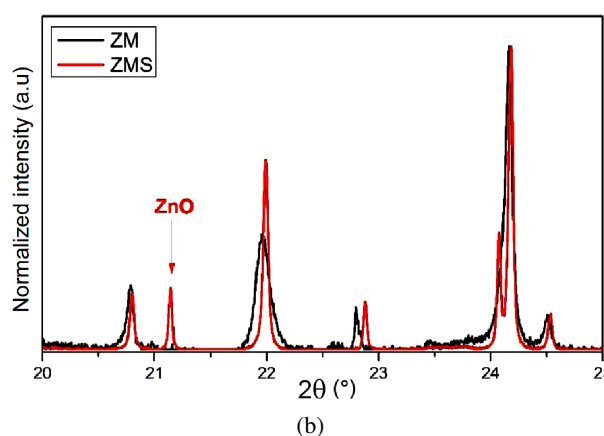
3.2. ZMC samples

Regarding the Zn-Mn-Cr oxide pigments, the X-ray powder diffractograms of the produced pigments can be seen in Fig. 4. The samples ZMC25 and ZMC50 consist of a phase mixture, indicating that the amount of chromium oxide was not enough to react with ZnMn_2O_4 and form a solid solution. These samples possibly have phases such as MnCr_2O_4 or ZnCr_2O_4 , among others.

The samples ZMC75 and ZMC100 present only the MnCr_2O_4 phase (with Zn^{2+} incorporated in the struc-



(a)



(b)

Figure 3. X-ray powder diffractograms of the ZM and ZMS samples (a) and selected 2θ region (b)

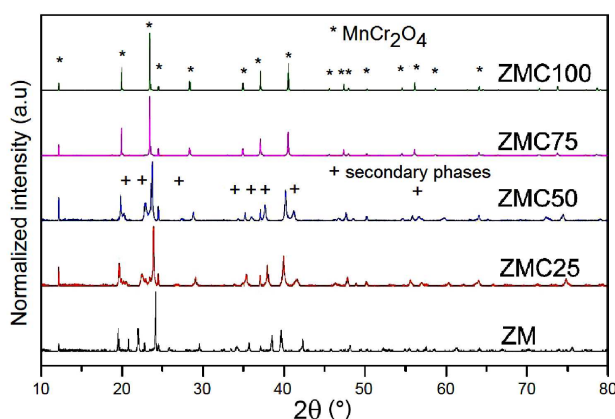


Figure 4. X-ray powder diffractograms of ZM and ZMC pigments with different Cr_2O_3 amounts

ture), with high purity. This phase is a spinel of cubic structure with symmetry $Fd\bar{3}m$ and cell parameters $a = b = c = 8.437 \text{ \AA}$ (JCPDF 75-1614). By looking more closely (inset in Fig. 5), it is possible to see that XRD pattern of the ZMC75 sample has broader peaks and shoulders, suggesting that the phase is not completely formed.

The spinel phase of the precursor ZM has Zn^{2+} ions at tetrahedral sites and Mn^{3+} at octahedral sites. However,

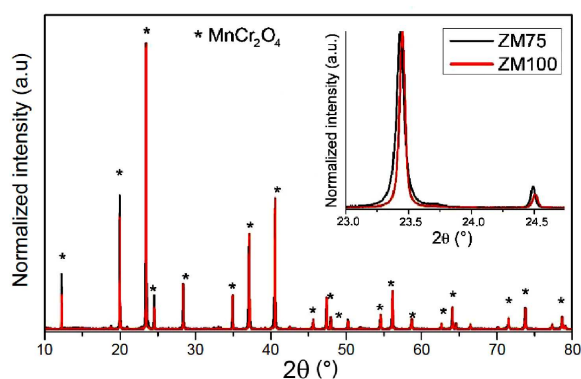
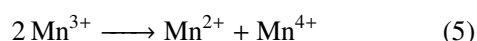


Figure 5. X-ray powder diffractograms of ZMC75 and ZMC100 samples

with addition of chromium, the Cr^{3+} (d^3) ions preferentially occupy octahedral sites, because of their higher stability at these sites (crystal field stabilization energy - CFSE) than the Mn^{3+} (d^4) ions. The Mn^{3+} is unstable and disproportionate (Eq. 5), generating Mn^{2+} (d^5) ions that migrate to the tetrahedral sites and Mn^{4+} (d^3) ions, which also have high CFSE at the octahedral sites. Thus, the presence of MCr_2O_4 type phases, where $\text{M} = \text{Zn}^{2+}$ or Mn^{2+} , is verified.



The absence of ZnO or other zinc-based phases suggests that the Zn^{2+} ions are at the tetrahedral sites of MnCr_2O_4 forming a mixed spinel such as $(\text{Mn,Zn})[\text{Mn,Cr}]_2\text{O}_4$. The presence of three Mn^{4+} ions at an octahedral site can be compensated by the formation of one chromium vacancy.

The samples ZMC25 and ZMC50 contain secondary phases, a bad result from a pigment point of view. With more secondary phases, more reactions can occur when the pigments are thermally treated; this reduces the thermal stability and produces poor quality coloured enamels with surface deformations.

Regarding the morphology (Fig. 6), all the ZMC samples presented particles smaller than $10 \mu\text{m}$, i.e. suitable for use as pigments. Inorganic pigments must be insoluble in glazes, with the most widely used particle sizes varying from 0.1 to $10 \mu\text{m}$, as stated by Monrós *et al.* [14].

The colorimetric coordinates of the powder pigments are shown in Table 3. Due to its composition (zinc, manganese, chromium, and iron oxides) and various crystalline phases present in this pigment (FeCr_2O_4 , ZnFe_2O_4 , or ZnCr_2O_4 and the secondary phase ZnO), the CBP produces a colour similar to ZCMS100. The ZMCS100 samples were prepared from pure reagents ZnO, MnO and Cr_2O_3 , with the same intermediary pro-

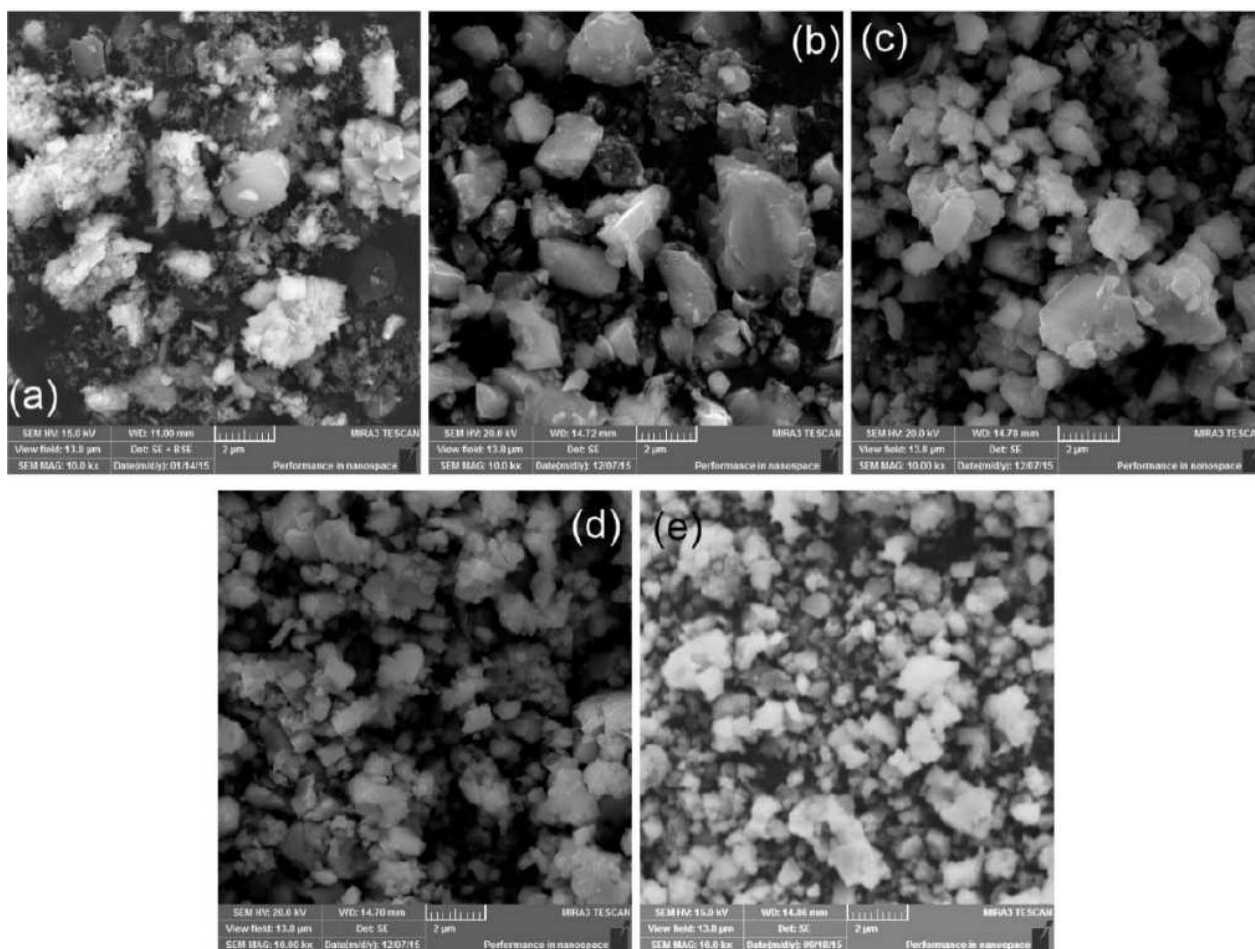


Figure 6. FE-SEM micrographs of pigments: a) ZM, b) ZMC25, c) ZMC50, d) ZMC75 and e) ZMC100

Table 3. CIE $L^*a^*b^*$ colorimetric coordinates of the powder pigments, enamelled pieces with two different frits and PMMA samples coloured with ZM and ZMC pigments

Sample	Powder			Frit F1 (1050 °C)			Frit F2 (850 °C)			PMMA		
	L^*	a^*	b^*	L^*	a^*	b^*	L^*	a^*	b^*	L^*	a^*	b^*
ZM	44.52	8.70	15.12	n.m.	n.m.	n.m.	26.16	5.42	4.51	36.46	15.33	10.37
ZMC75	33.77	8.93	9.12	n.m.	n.m.	n.m.	39.93	6.30	7.47	31.91	4.59	2.60
ZMC100	29.94	10.33	10.78	38.53	8.94	10.42	30.68	4.54	3.19	31.58	4.13	2.13
ZMS	37.05	5.79	10.28	n.m.	n.m.	n.m.	33.68	5.40	4.49	-	-	-
ZMCS100	35.5	14.50	15.29	n.m.	n.m.	n.m.	44.76	11.14	16.11	-	-	-
CBP [§]	40.29	19.97	14.70	-	-	-	43.53	14.27	6.84	-	-	-

n.m.: Enamelled piece with surface deformations was not measured. CBP[§]: commercial brown pigment

cessing used in samples with electrode material. These samples show low crystallinity when analysed by XRD, with wide peaks and presence of secondary phases, such as $ZnMnO_3$. The presence of mineralizers such as potassium in the samples derived from the batteries, e.g. ZMC100, contributes to the formation of the stable, crystalline phase and without the presence of secondary phases.

The CIE $L^*a^*b^*$ colorimetric coordinates and photos of the enamelled ceramics produced using two different frits are presented in Table 3 and Fig. 7, respectively. All the samples are brown and subtle changes occur in the colorimetric coordinates with increasing chromium oxide content. However, when compared with similar compositions (ZM x ZMS and ZMC100 x ZMCS100), the occurrence of colour changes is very clear; this could probably be due to the presence of secondary phases in the ZMS and ZMCS synthetic samples. All the enamelled pigments are stable at 850 °C (Fig. 7, Frit F2), but only ZMC100 was stable at high temperature (1050 °C) as shown in Fig. 7, Frit F1. This indicates that the precursor : Cr_2O_3 molar ratio of 1 : 1 produced the best pigment because it can be applied over

a wide temperature range. The presence of surface deformations on the enamelled ZMC75 piece (Fig. 7) can be associated with the aforementioned phases that are not completely formed and may also be due to the reaction/decomposition of compounds present in this pigment.

The CIE $L^*a^*b^*$ colorimetric coordinates and photos of the polymer (PMMA) coloured with the ZM (precursor) and ZMC pigments are presented in Table 3 and Fig. 8, respectively. All the ZMC samples, even the precursor ZM, presented good properties to be considered as pigments for polymers, such as high colouration, opacity, and compatibility with polymers and additives. Application in ceramics and polymers could be an alternative solution to ion immobilization [19], thus drastically reducing environmental contamination by incorrect disposal of batteries.

IV. Conclusions

The production of brown inorganic pigments using an electrode materials obtained from spent Zn-C batteries is a very interesting method for recycling toxic residues.

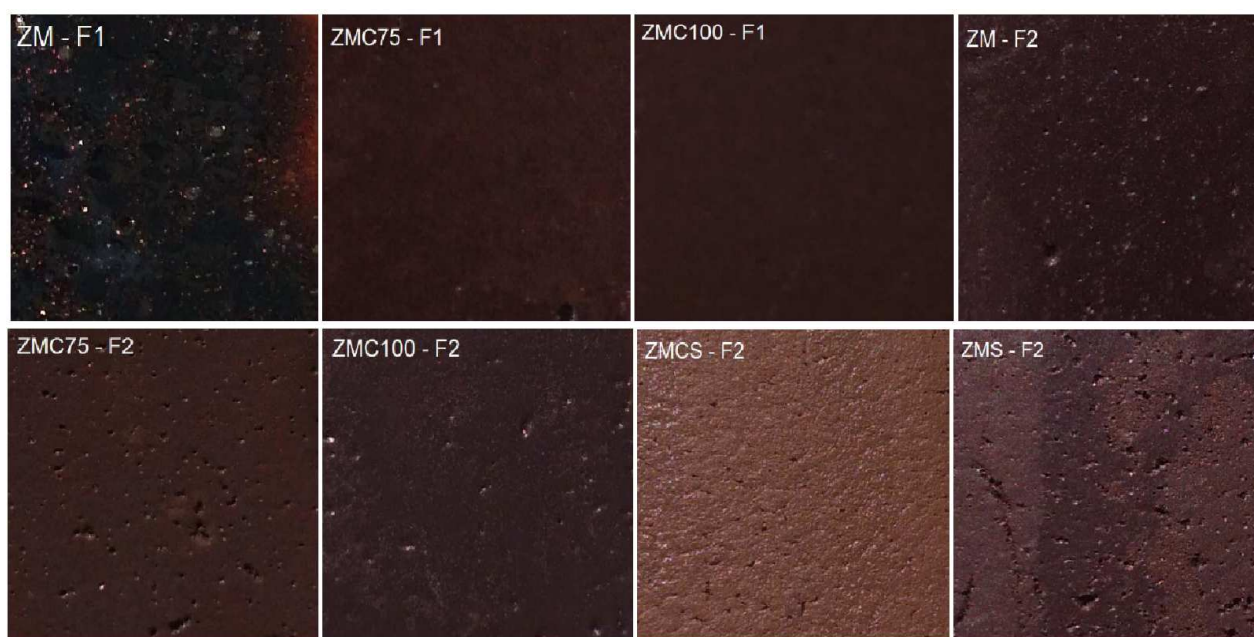


Figure 7. Ceramic pieces enamelled with frit F1 and F2



Figure 8. PMMA samples coloured with ZM and ZMC pigments

This is particularly important now as the production and disposal of spent batteries is constantly increasing, leading to environmental problem. The pigments produced in this study presented good properties for application in ceramics at 850 °C and in polymers. The ZMC100 sample displayed an advantage over other tested pigments; it can be applied for enamelling at 1050 °C, increasing the possibilities for its application.

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