Manganese oxide – antimony oxide – lead – lead dioxide vitrocermics

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Abstract

The number of spent batteries was increased significantly in recent years along with the use of mobile phones, vehicles, and other high-tech products. In this work the vitrocermics in the 5MnO2-xSb2O3(9Pb-x)Pb3O4 composition where x = 0 – 40 mol% Sb2O3 were synthesized by melt – quenching method using as raw materials the spent plates of a car battery (the anode as Pb source and cathode as PbO2 source), MnO2 and Sb2O3 powders. The prepared samples were characterized by XRD, IR and UV-Vis data. The electrochemical performances of the antimony – manganese – lead materials used as working electrodes at a car battery were demonstrated by measurements of cyclic voltammetry. The combined results from varied techniques show that antimony ions play the important role in the conductive and electrochemical properties.

Motivation

An approach to improve the performance of the recycled electrodes provided from spent car battery using MnO2 and Sb2O3 as additive in view of new applications in the renewable batteries.

Experimental procedure

Samples were prepared by melt quenching method using as starting materials spent electrodes from a disassembled car battery as sources of PbO2 and Pb (in 9 : 1 molar ratio) mixed in suitable proportions with 5 mol% MnO2 and x mol % Sb2O3 powders. The mixtures were melted in sintered corundum crucibles at 1300 °C, in an electric furnace. After 10 minutes the molten material was quenched at room temperature by pouring it onto a stainless-steel plate. The recycled and manganese-antimony doped samples were characterized by the analysis of X-ray diffraction (XRD). The FT-IR spectra of the samples were obtained in the 350-1500 cm\(^{-1}\) spectral range with a JASCO FTIR 6290 spectrometer using the standard KBr pellet disc technique. UV-VIS and cyclic voltammetry (VC) measurements. A potentiostat / galvanostat tip AUTOLAB PGSTAT 302N (EcoChemie, Netherlands) and the NOVA 1.11 software were used to test the cyclic voltammograms of the electrode material. Discs of obtained samples were used as working electrode, platinum as counter electrode, saturated calomel electrode as reference electrode and sulfuric acid solution as liquid electrolyte. All experiments were conducted in a solution of H\(_2\)SO\(_4\) with the concentration of 38%, in agreement with the electrolyte solution used in the lead acid batteries.

Results and discussion

The \(X\) - ray patterns of studied samples (Figure 1a) indicate the presence of the \(\text{PbO}_2\bullet\text{PbSO}_4\) crystalline phase with monoclinic structure and metallic Pb with cubic structure for samples with \(x \leq 15\) mol\% \(\text{Sb}_2\text{O}_3\). By addition of lower \(\text{Sb}_2\text{O}_3\) content up to 15 mol\% in the vitrocermic network the amount of these crystalline phases were decreased. For the samples with \(x > 20\) mol\% \(\text{Sb}_2\text{O}_3\) an amorphous structure were evidenced. The compositional evolution of the IR spectra (Figure 2) shows the following structural modifications by doping \(x\) : the decrease of intensity of the IR bands situated at 600, 1050 and 1150 cm\(^{-1}\) due to the sulfate units; \(i\) the appearance of new IR bands situated in the region between 750 and 960 cm\(^{-1}\) corresponding to the \(\text{PbSO}_4\) structural units with \(n = 3, 4\) and \(5\) for samples with higher \(\text{Sb}_2\text{O}_3\) contents over 15 mol\%; \(ii\) an increasing trend of the IR bands located between 950 and 1250cm\(^{-1}\) towards higher wavenumbers and enriched intensities at higher dopant level. By doping the excess of oxygen atoms can be accommodated in the host matrix by the formation of \(\text{PbSO}_4\) structural units (with \(n = 3, 4\) and \(5\)) and \(\text{Sb}_2\text{O}_3\) structural units (IK band centered at about 600 cm\(^{-1}\)).

UV-VIS data show an intense band centered at about 310 nm corresponding to the electronic transitions due to the \(\text{Pb}^{2+}\) ions (see Figure 3). By doping the intensity of this band was decreased. This evolution suggests that for higher dopant level, the modifications take place in the host matrix related mainly to the \(\text{PbSO}_4\) and \(\text{PbS}_2\text{O}_3\) structural units. Cyclic voltammograms illustrated in Figure 4 show much more formed the oxidation and reduction waves for the sample with 30 mol\% \(\text{Sb}_2\text{O}_3\) compatibly with undoped sample.

Conclusions

In this study, a series of new \(x\text{Sb}_2\text{O}_3\bullet\text{MnO}_2\bullet\text{Pb}_3\text{O}_4\) glasses and glass ceramics with \(x = 0 - 40\) mol\% \(\text{Sb}_2\text{O}_3\) were prepared by melt-quenching method using as raw materials the spent plates of a car battery. Their structure, optical and electrochemical properties were investigated by XRD, FTIR and UV-VIS spectroscopy and cyclic voltammetry measurements. XRD data reveal the presence of \(\text{PbSO}_4\text{Pb}_2\text{O}_5\) crystalline phase with monoclinic structure in the vitrocermics with \(x \leq 15\) mol\% \(\text{Sb}_2\text{O}_3\). By increasing of the dopant level up to 20 mol\% \(\text{Sb}_2\text{O}_3\) an amorphous structure can be evidenced. IR data show the decrease of sulfate units and the formation of \(\text{PbSO}_4\) structural units with \(n = 3, 4\) and \(6\) by adding of \(\text{Sb}_2\text{O}_3\) contents in the host matrix. The intensity of the UV-Vis band centered at about 310 nm due to the free \(\text{Pb}^{2+}\) ions were decreased by doping, in agreement with IR data (the high-coordinated lead atoms were increased). Recycled and manganese-antimony samples show electrochemical performances.

References


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