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Recycled and antimony-doped lead materials: XRD, SANS and voltammetric study

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Abstract. In the last ten years the production of lead grills from automotive batteries has been replaced by lead alloys with other metals such as antimony. This work describes antimony-lead materials that contain a substantial amount of 10 mol% Sb_2O_3 and varied compositions between Pb : PbO_2. The sources of PbO_2 (cathodic electrode) and Pb (anodic electrode) come from spent plates of a car battery. The recycled and antimony-doped materials were characterized by the analysis of X-ray diffraction and Small Angle Neutron Scattering (SANS) data. The electrochemical performances of the antimony-lead materials used as working electrode at a battery were demonstrated by measurements of cyclic voltammetry.

Introduction. Until today, there are still many problems that must be solved through innovative research to make the recycling of spent lead-acid batteries and the separation of Pb - Sb alloy more environmentally friendly and energy-saving. In this paper, a novel method for regenerating lead paste, by melt-quenching method with separation of electrode material consisting to the lead and stibiu crystalline phase was developed.

Experimental procedure. Raw materials: anodic (Pb source) and cathodic (PbO_2 source) electrode of a spent automotive battery and Sb_2O_3 powder. The crucibles with the weighed mixture in the $10Sb_2O_3 \cdot 90[xPbO_2 \cdot yPb]$ composition where PbO_2 : Pb = 2 : 8, 3 : 7, 7 : 3 and 8 : 2 were placed in an electric oven, set at a temperature of 900 °C. After 10 minutes, the crucible with the melt was removed from the oven and quickly poured onto a stainless steel plate at room temperature.

RESULTS DISCUSSION

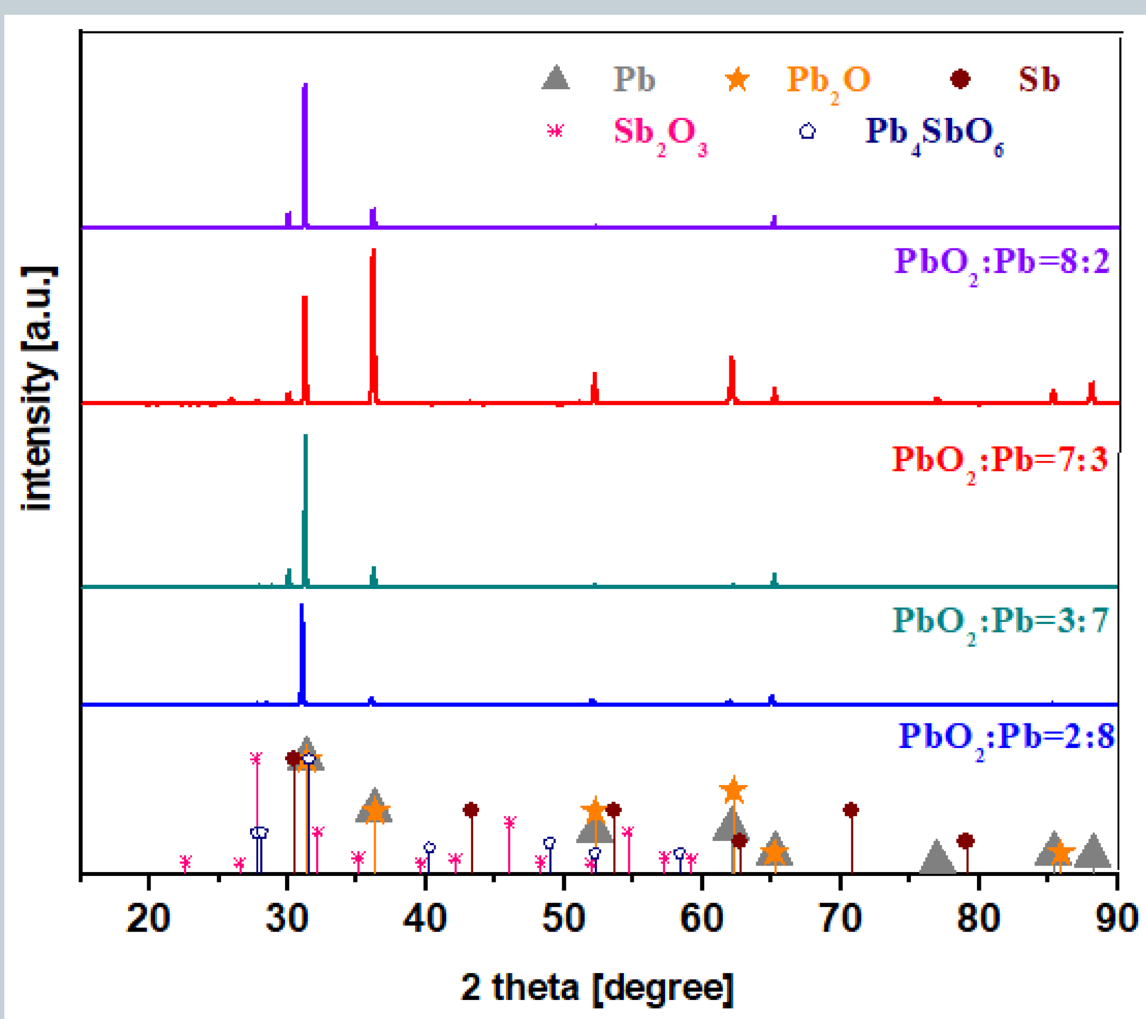

Figure 1: a) X-ray patterns of the recycled and antimony-doped materials in the $10Sb_2O_3 \cdot 90[xPbO_2 \cdot yPb]$ composition where PbO_2 : Pb = 2 : 8, 3 : 7, 7 : 3 and 8 : 2.

Table 1: Structural parameters of investigated system based on SAS codes using analytical approximation model of particles shape namely Guinier-Porod model (where Rg represents gyration radius and s – Porod exponent) from 0.01 Å to 0.6 Å.

Guinier – Porod model				
PbO_2 : Pb ratio	8 : 2	2 : 8	7 : 3	3 : 7
Gyration radius, R_g [Å]	24.296	21.589	26.168	189.59
s	2.1605	2.2749	2.132	$7.68 \cdot 10^{-6}$
Porod exponent	3.7834	3.4858	3.7936	2.9193

X-ray diffractograms of the system recycled from the electrodes of a spent car battery and doped with antimony (III) oxide in the $10Sb_2O_3 \cdot 90[xPbO_2 \cdot yPb]$ composition where PbO_2 : Pb = 2 : 8, 3 : 7, 7 : 3 and 8 : 2 are shown in ***Figure 1***. All samples have a vitroceramic structure. Five crystalline phases in varied amounts were found in the XRD data, namely: metallic Pb crystalline phase with cubic structure (the diffraction peak centered at 31.3° with 100% intensity), Pb2O crystalline phase with cubic structure, Sb, Sb2O3 and Pb_4SbO_6 crystalline phase. For the sample with *PbO_2 : Pb = 7 : 3* the peak corresponding to the Pb and Pb2O crystalline phase s increases in intensity, attaining a maximum value.

The nanoscale inhomogeneities in the studied samples can be evidenced from ***SANS data***. Reproduction of the scattering data was made using shape independent modeling by the Guinier-Porod model. The Guinier - Porod empirical model will be used to fit scattering data from asymmetric objects such as shapes intermediate spheres. The SANS curves fitting with the Guinier - Porod model in the logarithmic coordinates for studied systems are depicted in ***Figure 2***. A inspection of the SANS curves shows that the microstructure depends on the PbO_2 : Pb molar ratio because appears modifications of position of the bands located at small Q. A charge in slope of the SANS curve suggests varied regimes characterized by different length scales. Fit of the Guinier - Porod model to the experimental SANS data corresponding to the studied samples allow a good adjust for the samples with PbO_2 : Pb = 2 : 8, 7 : 3 and 8 : 2 molar ration. The values of Porod exponent, s, evidenced in ***Table 1*** are varied from s < 1 (for the sample with PbO_2 : Pb = 3 : 7) to 2.2749 (for the sample with PbO_2 : Pb = 2 : 8). For elongated structures [1] are known a fit with an exponent Porod of s < 1. This observation suggests that the samples with PbO_2 : Pb = 3 : 7 is elongated structure while the samples with PbO_2 : Pb = 2 : 8, 7 : 3 and 8 : 2 correspond to the compacted structures.

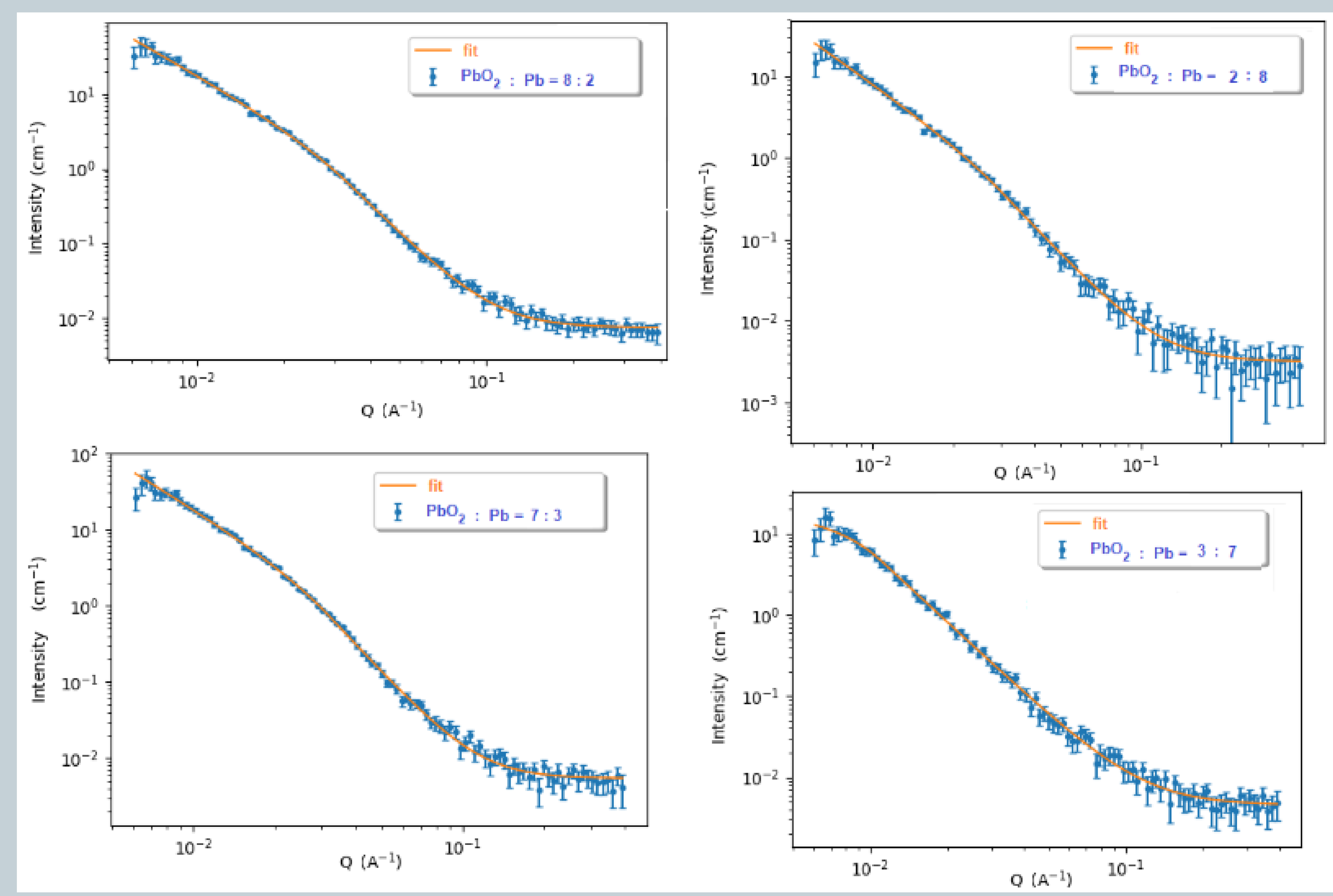

Figure 2: SANS curves of the recycled and antimony-doped materials in the $10Sb_2O_3 \cdot 90[xPbO_2 \cdot yPb]$ composition where PbO_2 : Pb = 2 : 8, 3 : 7, 7 : 3 and 8 : 2.

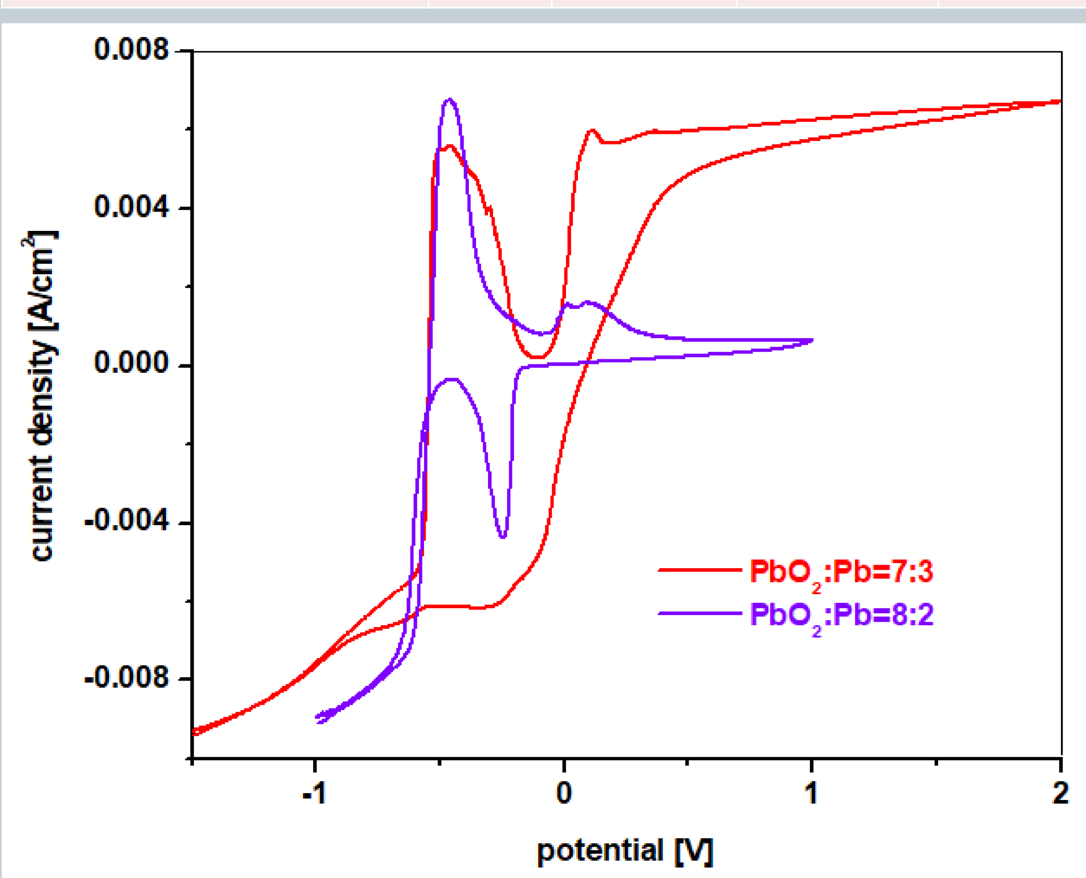

Figure 4: Cyclic voltammograms of the recycled and antimony-doped materials in the $10Sb_2O_3 \cdot 90[xPbO_2 \cdot yPb]$ composition where PbO_2 : Pb = 7 : 3 and 8 : 2.

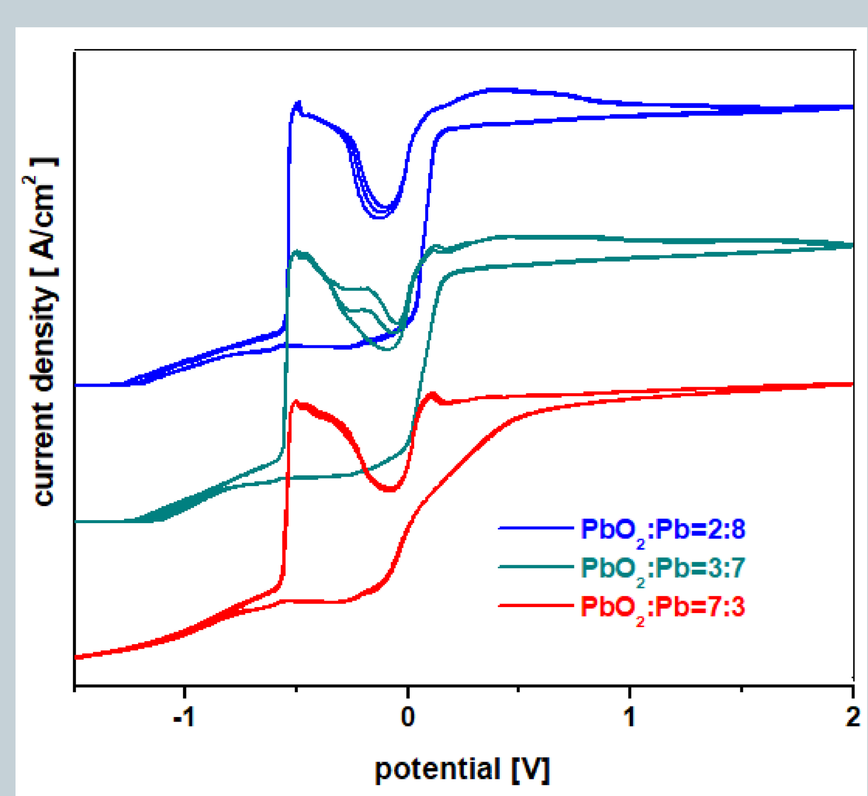

Figure 5: Cyclic voltammograms scanned after three cycles of the recycled and antimony-doped materials in the $10Sb_2O_3 \cdot 90[xPbO_2 \cdot yPb]$ composition where PbO_2 : Pb = 2 : 8, 3 : 7 and 7 : 3.

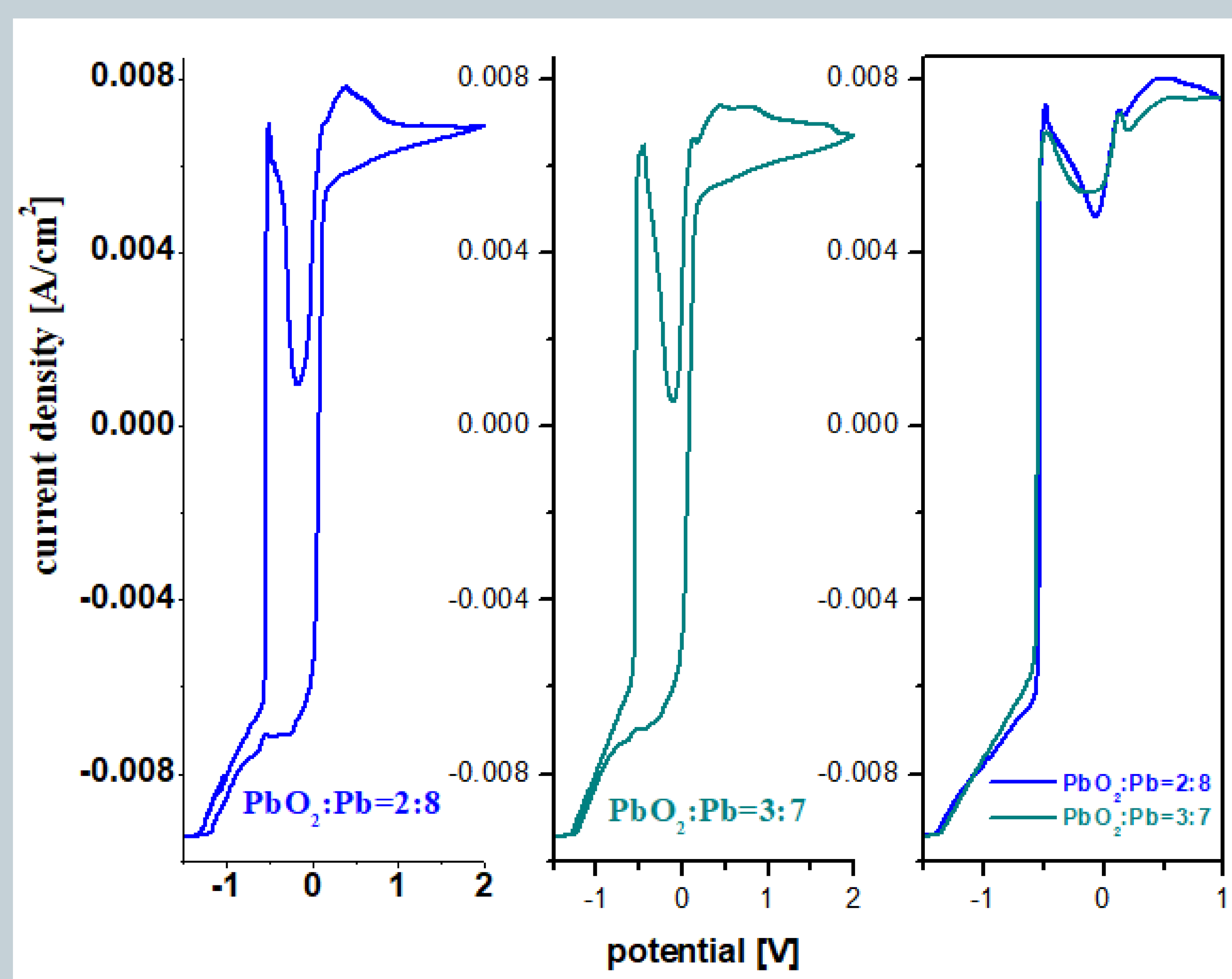

Figure 3: Cyclic voltammograms and linear scanning voltammograms of the recycled and antimony-doped materials in the $10Sb_2O_3 \cdot 90[xPbO_2 \cdot yPb]$ composition where PbO_2 : Pb = 2 : 8 and 3 : 7.

The electrochemical performance of recycled materials and doped with antimony (III) oxide, as working electrodes on the car battery, was investigated by measurements of cyclic voltammetry and ***linear scanning voltammetry***. The electrochemical properties of the samples obtained were tested by ***cyclic voltammetry measurements*** using an AUTOLAB PGSTAT 302N potentiostat / galvanostat (EcoChemie, The Netherlands) and NOVA 1.11 software. To simulate the behavior of the electrode in the car battery was used an electrochemical cell with three electrodes: the reference electrode - calomel, the working electrode (recycled and antimony-doped sample), counter electrode (platinum electrode) and calomel electrode (reference electrode) which are all immersed in a solution of 38% concentration of sulphuric acid. Cyclic voltamograms of electrode materials in the composition $10Sb_2O_3 \cdot 90[xPbO_2 \cdot yPb]$ composition where PbO_2:Pb = 2 : 8, 3 : 7, 7 : 3 and 8 : 2 are shown in ***Figures 3 and 4***. The oxidation peak located at -0.54V comes from the overlap of two waves, one located at -0.54V corresponding to the redox system $HPbO_2^-$/Pb and the other centered at -0.58V due to the PbO/Pb redox process [2]. The inspection of linear scanning voltammograms indicates that the current density increases slowly for the sample with PbO_2 : Pb = 2 : 8. The doping with a suitable level of PbO2:Pb ratio, respectively PbO_2 : Pb = 7 : 3 removes the passivation phenomena and hydrogen evolution reactions and the intensity of the residual current increases in the range 0 and 2V. The high degree of irreversibility of cyclic voltammograms of electrode materials with PbO_2 : Pb = 2 : 8 and 3 : 7 (see ***Figure 5***) due to the presence of oxygen evolution reactions and dimerization reactions of sulfate ions, yielding the change of the electrolyte concentration and the disadvantage that upon the discharging of the battery.

Conclusions: The purpose of this work was to justify the induced structural modifications of the increase of PbO_2:Pb ratio in recycled and antimony-doped materials and to explore the structural role of doping level. The local structure of the obtained samples in the $10Sb_2O_3 \cdot 90[xPbO_2 \cdot yPb]$ composition where PbO_2 : Pb = 2 : 8, 3 : 7, 7 : 3 and 8 : 2 was characterized by the analysis of X-ray diffraction (XRD) and Small Angle Neutron Scattering (SANS) data. The gyration radius in the Guinier - Porod model have values situated in the range between 21.589 and 26.168 Å for the samples with PbO_2 : Pb = 2 : 8, 7 : 3 and 8 : 2 while by the adding of PbO_2 : Pb = 3 : 7 molar ratio the value were increased abruply. The result shows large modifications in this sample having an elongated structure. The electrochemical performances of the prepared materials were tested from cyclic voltammetry and linear scanning voltammetry measurements. The best reversibility of the cyclic voltamogram was obtained for the sample with PbO_2 : Pb = 7 : 3 which is why we recommend it as ideal in applications as an electrode for renewable batteries, although it has a slightly lower current density than its analogues with a lower amount of dopant. Recycled and antimony-doped electrodes can be reused as new energy sources in batteries.

References: 1. S. Rada, R.V. Erhan, V. Bodnarchuk , L. Barbu-Tudoran , E. Culea, J. Alloys Compounds 882 (2021) 160721. 2. S. Rada, M. Unguresan, M. Rada, C. Tudoran, Jiaou Wang, E. Culea, J. Electrochem. Soc. 167 (2020) 090548.

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