BULGARIAN ACADEMY OF SCIENCES
INSTITUTE OF ELECTROCHEMISTRY AND ENERGY SYSTEMS "ACADEMICIAN EVGENI BUDEVSKI"

IOCN 2020 2nd International Online-Conference on Nanomaterials
15–30 NOVEMBER 2020 | ONLINE
nanomaterials MDPI

Synthesis of nanosized powders for lead-acid battery pastes by recycling of used batteries

Mariela Dimitrova*, Sasho Vassilev
Institute of Electrochemistry and Energy Systems, Bulgarian Academy of Sciences, Sofia, Bulgaria
*mariela.dimitrova@iees.bas.bg

Introduction:

Recently, with the entry of the new millennium, for the production of lead-acid batteries, the use of secondary refined lead reached 60-66% of the total lead [1]. Recycling used lead batteries saves natural resources, consumes less energy to produce lead, and significantly avoid air and water pollution. The hydrometallurgical methods of batteries recycling is more widely used [2, 3]. They involve the oxidation of lead waste by treatment with Na_2CO_3, $(NH_4)_2CO_3$ or NaOH. The received lead carbonate, hydroxide or hydroxycarbonate is subjected to pyrometallurgical treatment at lower temperatures (400-650°C) compared to pyrometallurgical methods (900-1400°C) [4-6]. In recent years, researches has been based on the need to develop an efficient, low-cost environmental technology for recycling waste lead paste. Experiments to extract Pb from used lead paste by treatment with aqueous citric acid solution lead to the generation of a lead citrate precursor, which can easily be converted to PbO for direct production of lead pastes for batteries Controlling the calcination process may lead to variations in the microstructure and the formation of micro to nanosized powders – a new perspective in the development of lead-acid battery technology [7, 8].

Purpose: Finding an optimal method for recycling of used lead-acid batteries in order to:
- recover lead from positive (PAM) and negative (NAM) active masses;
- obtain lead oxide powders for direct application in the formation of lead pastes.

Experimental:

Desulfurization and leaching were performed in one step by adding simultaneously aqua $C_6H_5Na_3O_7.2H_2O$ *(0.5 mol/l)* and $C_6H_8O_7$ (0.8 mol/l, 1 mol/l) solutions at varying temperatures (25-100°C) and heat treatment time (1-2h). The ratio $PbSO_4$: $C_6H_5Na_3O_7.2H_2O$: $C_6H_8O_7$ is 1: 2.5: 2.5. Hydrogen peroxide is added to the samples of the positive active masses as a reducing agent for the conversion of Pb (IV) to Pb (II) as the ratio of sample: acid solution: peroxide is 1:1.5:2. Initially, the experiments were conducted with chemical purity substances (PbO_2, $Pb(NO_3)_2$ and $PbSO_4$) and lead oxide powder (85,7% PbO/14,3% Pb) for determining the appropriate conditions to prevent the lead losses at its recovery. The recycled spent positive and negative active masses have a chemical composition: NAM - *68.9% $PbSO_4$; 24.56% Pb; 2.98% PbO*; PAM – 33,08% *$PbSO_4$; 66,37% PbO_2.*

Results:

X-ray diffraction analysis (XRD)

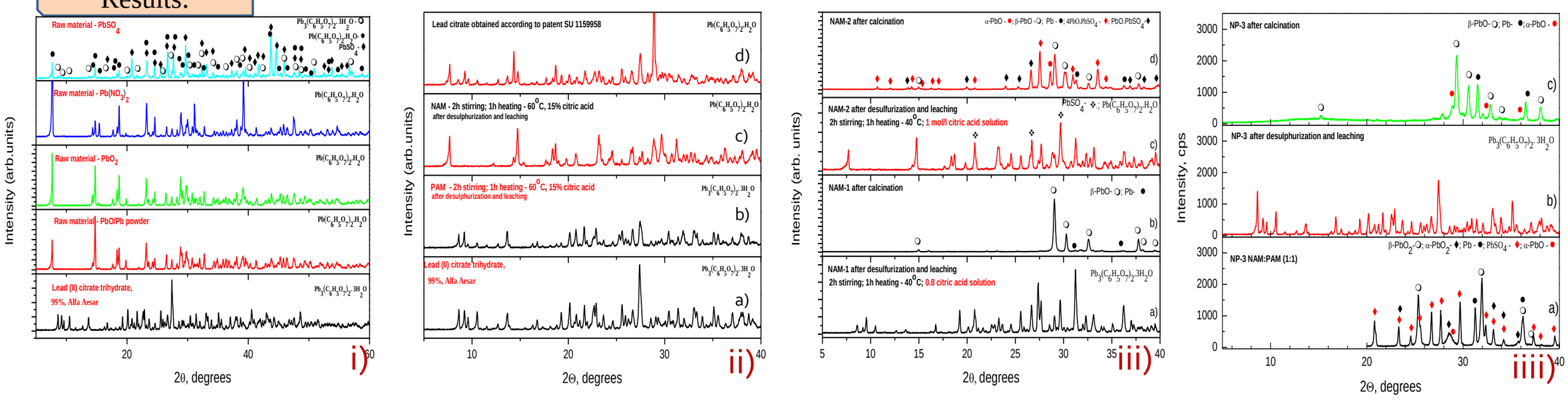

Figure 1. XRD diagrams of synthesized lead citrate: i) from chemically pure substances; ii) from spent active masses (PAM (b) and NAM (c)) of lead-acid batteries compared with chemically pure lead citrate trihydrate (a) and lead citrate obtained under patent SU 1159958 (d) (lead citrate obtained from lead nitrate , citric acid solution and ammonia) [9] ; iii) negative active mass depending on the concentration of the citric acid solution after desulfurization and leaching (a, c); after calcination (b, d); iiii) a mixture of used positive and negative active mass: (a) before recycling; b) after desulfurization and leaching; c) after calcination.

Differential Thermal Analysis (DTA/TG)

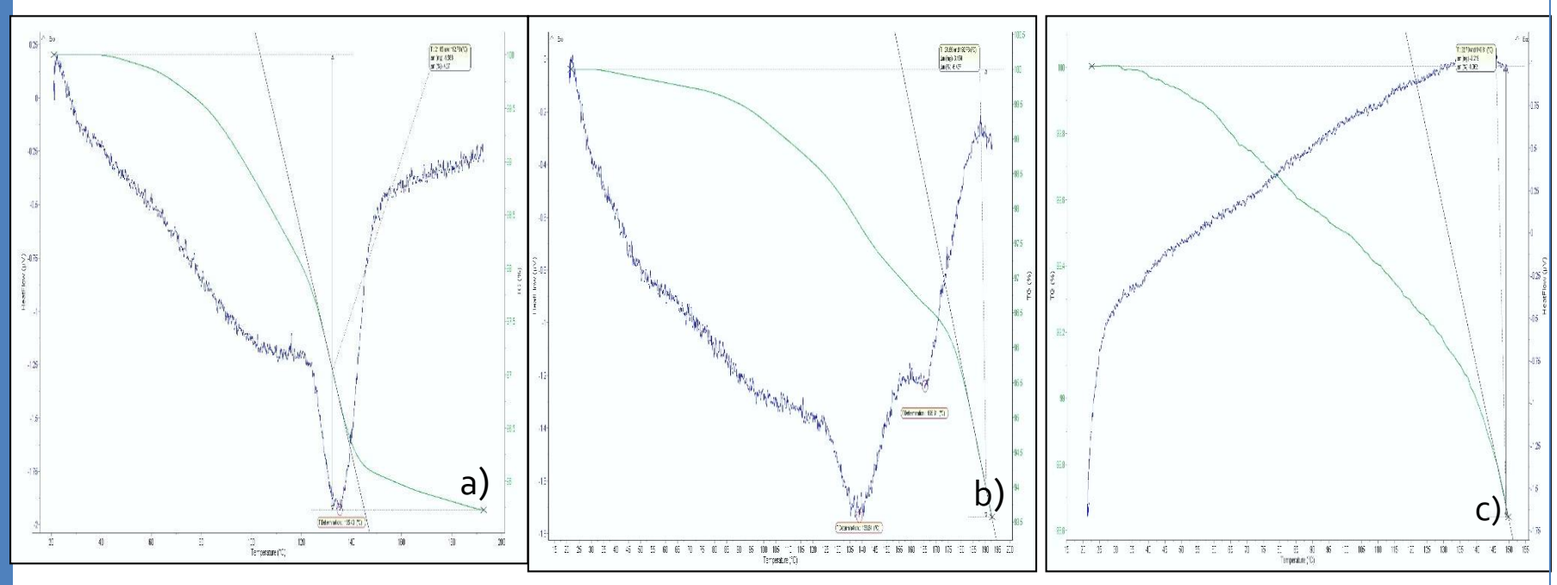

Figure 2. DTA /TG analysis of lead citrate: a) Pb3 (C6H6O7) 2.3H2O (c. p.); b) synthesized by PAM desulfurization and leaching; (c) synthesized from chemically pure Pb(NO3)2.

Scanning Eectron Microscopy (SEM)

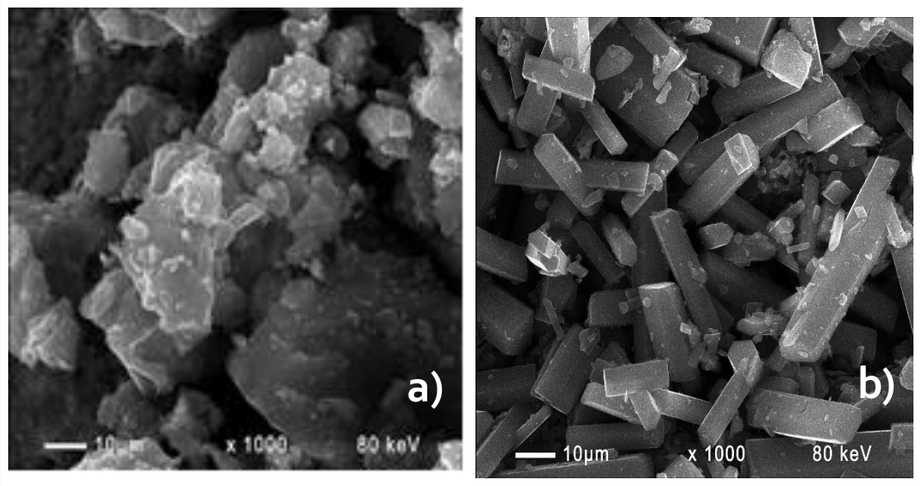

Figure 3. SEM images of lead citrate precursor *synthesized by desulfurization and leaching* of:
a) a used PAM; b) a mixture of used PAM and NAM .

Conclusions:

- **Two types of lead citrate precursor were obtained - $Pb(C6H5O7)2.H2O$ and $Pb3(C6H5O7)2.3H2O$);**
- **Finely dispersed lead oxide powders are obtained for use in the production of battery pastes by recycling;**
- **The measured crystallite sizes of the two main phases are: β-$PbO_{(111)}$ – 30-50nm and $Pb_{(111)}$ – 40 - 60nm, respectively.**

Acknowledgments

The authors thank Mrs. R. Andreeva for her technical assistance. This work was supported by the National Scientific Program NNP "Low Carbon Energy for Transport and Households - Eplus"

References:

1. Wei Zhang et. al., Renewable and Sustainable Energy Reviews 61 (2016) 108–122.
2. Rabah M.A., Barakat, M.A., Renew. Energy 23 (3–4), 2001 561–577.
3. Z. Vaysgant et. al. J. Power. Sources 53 1995 303–306.
4. R.D. Prengaman, H. McDonald, U.S. Patent 4,229,271 (October, 1980).
5. R.D. Prengaman, JOM 47 (1995) 31–33.
6. N. Lyakov et.al., Yearbook - VHTI, XXXI, 3, 1992, 36-45. (in bulgarian)
7. Sonmez, M.S., Kumar, R.V, Hydrometallurgy 95, 2009a (1–2), 53–60.
8. Sonmez, M.S., Kumar, R.V., *L*, Hydrometallurgy 95 (1–2) 2009b, 82–86;
9. Shklover L.P., Chicherina G.P., Serebrennikova G.M., Krasilshtik V.Z., SU 1159958 A, 1985. (in russian)