

Calcium oxide - lead lead dioxide vitroc ceramics

D. N. Piscoiu¹, S. Rada^{1,2}, S. Macavei², H. Vermesan¹, and E. Culea¹

¹Technical University of Cluj-Napoca, Faculty of Materials and Environmental Engineering, 400641, Cluj-Napoca, Romania

²National Institute for Research and Development of Isotopic and Molecular Technologies, 400293, Cluj-Napoca, Romania

Today the number of automobile is increased and as a result the need of lead acid batteries is highly. It is expected that the improvements made in the recycling of car batteries to imply the elimination of the disadvantages related to the traditional recycling methods. The purpose of this work is: i) to recycle the spent plates from a car battery by an eco-innovative method which provides an efficient desulfatization of the active mass from high wear plates of a car battery; ii) to characterize of prepared materials and to test of their electrochemical performances for the applications as new electrode for batteries. The recycled system in the $x\text{CaO} \cdot (100-x)[4\text{PbO}_2 \cdot \text{Pb}]$ composition where $x = 0 - 30$ mol% CaO was synthesized by melt quenching method. Samples prepared using as starting materials the spent plates provided from a car battery were investigated by the analysis of X-ray diffraction (XRD), InfraRed (IR) and UltraViolet-Visible (UV-Vis) spectroscopy and measurements of Cyclic Voltammetry and Linear Sweep Voltammetry. The X-ray diffractograms indicate two lead sulphated crystalline phases which by doping with higher CaO contents are partially transformed into the $\text{Ca}_3(\text{SO}_3)_2\text{SO}_4$ crystalline phase. By adding of higher CaO levels in the host matrix do not changes the intensity of the sulphate and sulphite IR bands. The formation of sulphito-sulphated phase of calcium ions is an advantage of this method over pyrometallurgic technique because our results indicate that lead sulphate does not decompose producing the sulfur oxides emissions in the atmosphere. The sulphate and sulphite ions are captured by the calcium ions. Measurements of cyclic voltammetry recommend the sample with $x = 30$ mol% CaO as suitable electrode material for the applications of the batteries.

Motivation

Recycling used batteries is an imperative aspect of sustainable development, which helps to conserve the environment; saving resources; reducing the volume of waste and brings economic benefits.

Results and discussion

XRD data analysis for the prepared system highlights in the host matrix **two sulphated phases of lead**: the PbSO_4 crystalline phase with orthorhombic structure and crystalline phase PbOPbSO_4 with monoclinic structure. By growing the content of calcium oxide in the host matrix appears a new crystalline phase, phase crystalline $\text{Ca}_3(\text{SO}_3)_2\text{SO}_4$ with monoclinic structure.

IR data indicates that there is no change in calcium oxide doping drastic intensity of the bands assigned to the sulfate bands, respectively those from 600 cm^{-1} and 1060 cm^{-1} which suggests the formation of the sulfite-sulphated phase of calcium.

UV-Vis data indicates an increase in the number of Pb^{+2} ions and a decrease in the number of sulfite ions from the host matrix by doping with high dopant contents up to 30 mol%.

The VC and VL measurements it results that the recycled material and doped with 30% moles CaO is suitable as a **new electrode for rechargeable batteries** as well lead acid battery.

Samples in the vitreous system with the composition: $x\text{CaO} \cdot (100-x)[4\text{PbO}_2 \cdot \text{Pb}]$ where $x = 0, 5, 10, 15, 30$ moles of CaO

were prepared by melt quenching method, using as starting materials the **anode and cathode of a used car battery and CaO powder**.

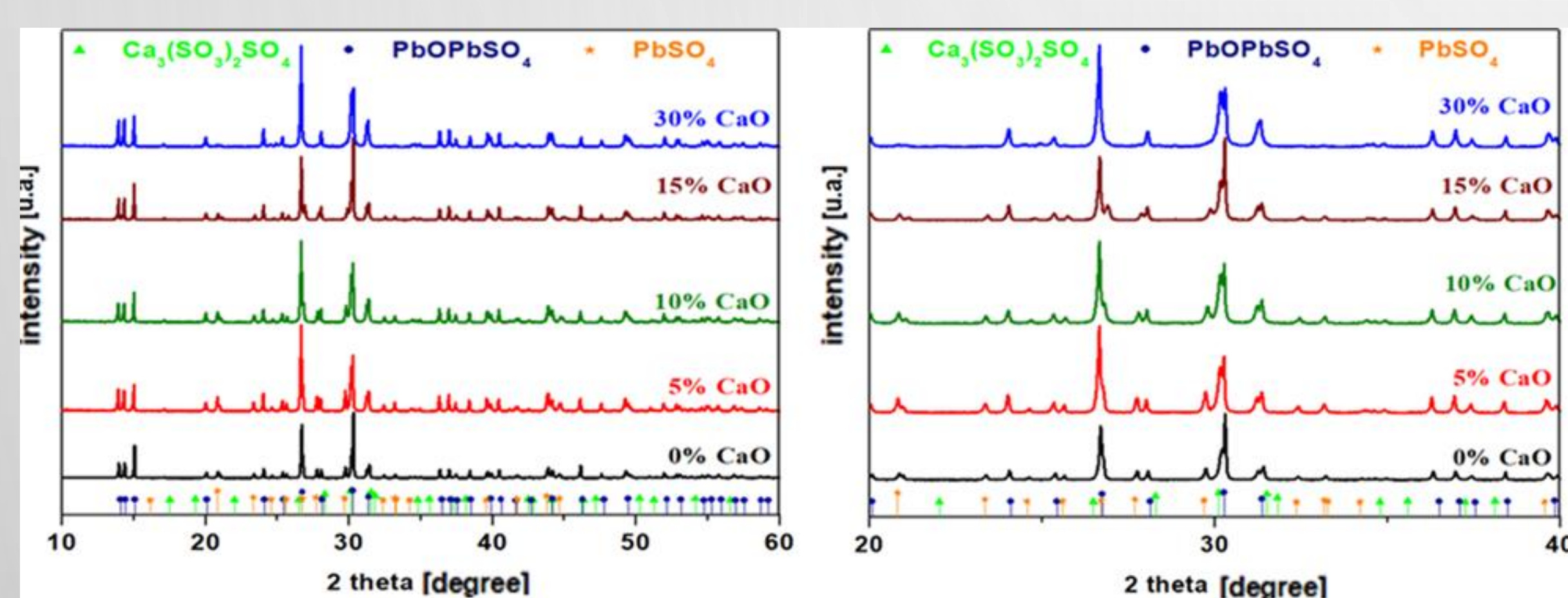
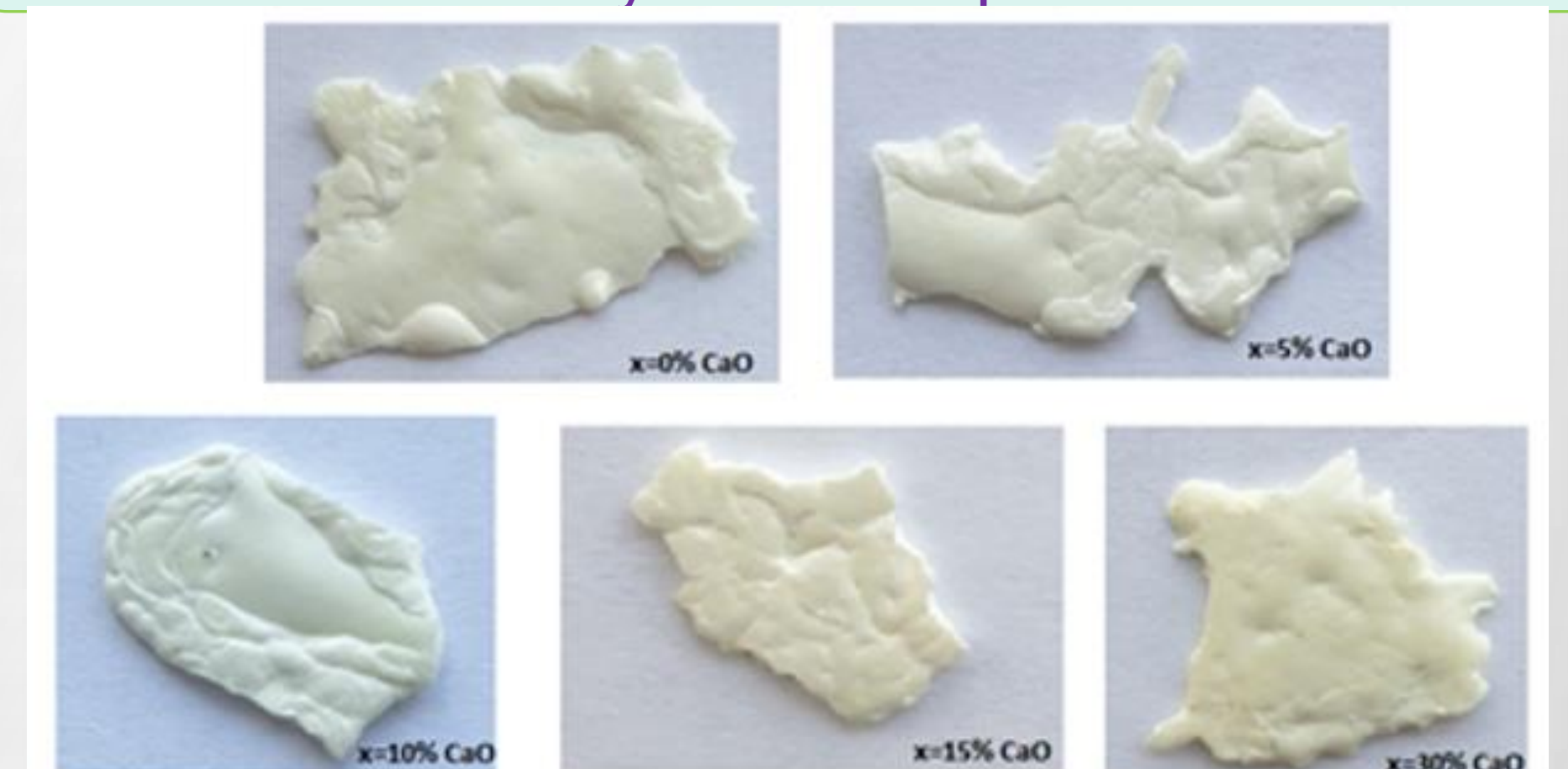


Fig. 1. X-ray diffractograms of recycled vitreous systems in the $x\text{CaO} \cdot (100-x)[4\text{PbO}_2 \cdot \text{Pb}]$ composition where $x = 0 - 30$ mol% CaO

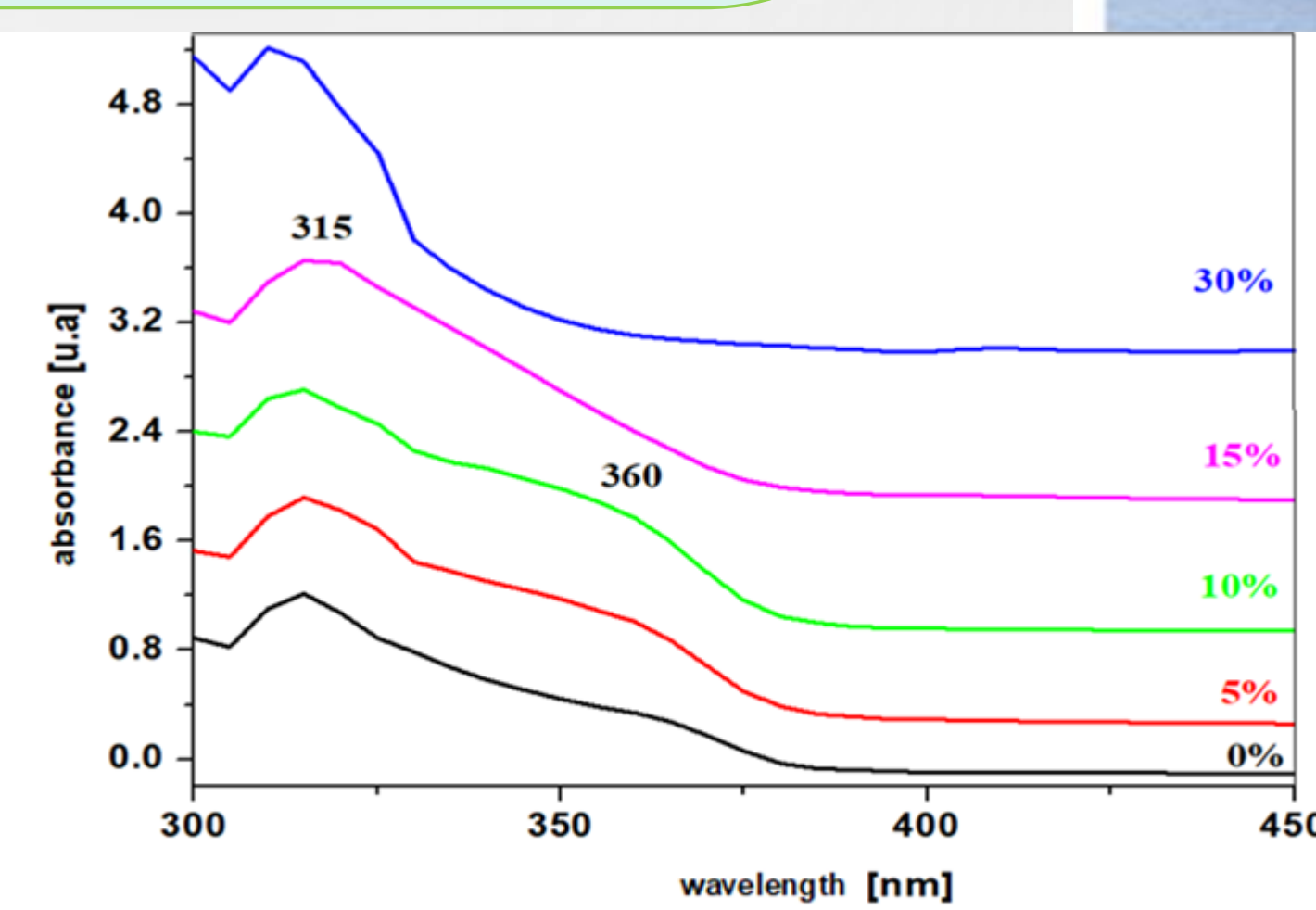


Fig. 3. UV-Vis spectra of recycled vitreous systems in the $x\text{CaO} \cdot (100-x)[4\text{PbO}_2 \cdot \text{Pb}]$ composition where $x = 0 - 30$ mol% CaO

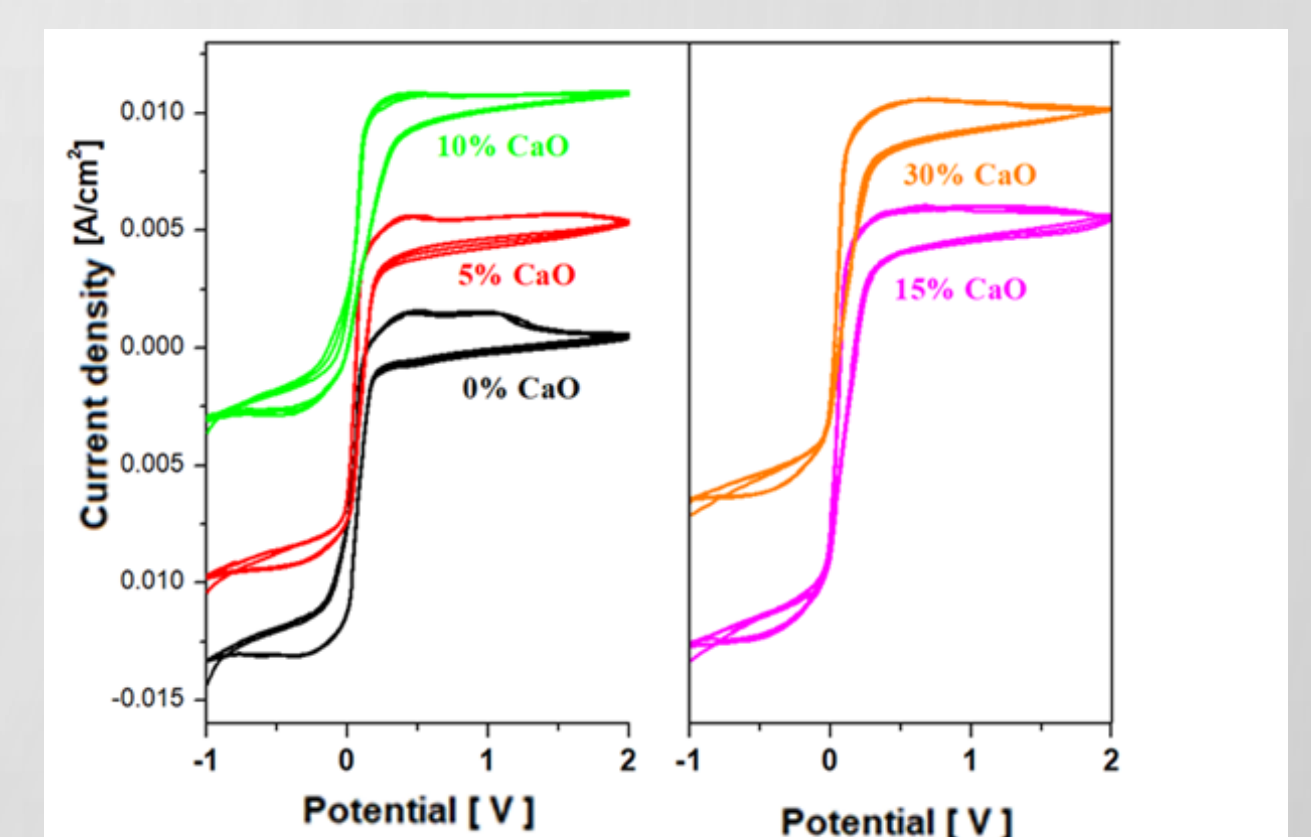


Fig. 5. Cyclic voltammograms of recycled vitreous systems in the $x\text{CaO} \cdot (100-x)[4\text{PbO}_2 \cdot \text{Pb}]$ composition where $x = 0 - 30$ mol% CaO, after three cycles

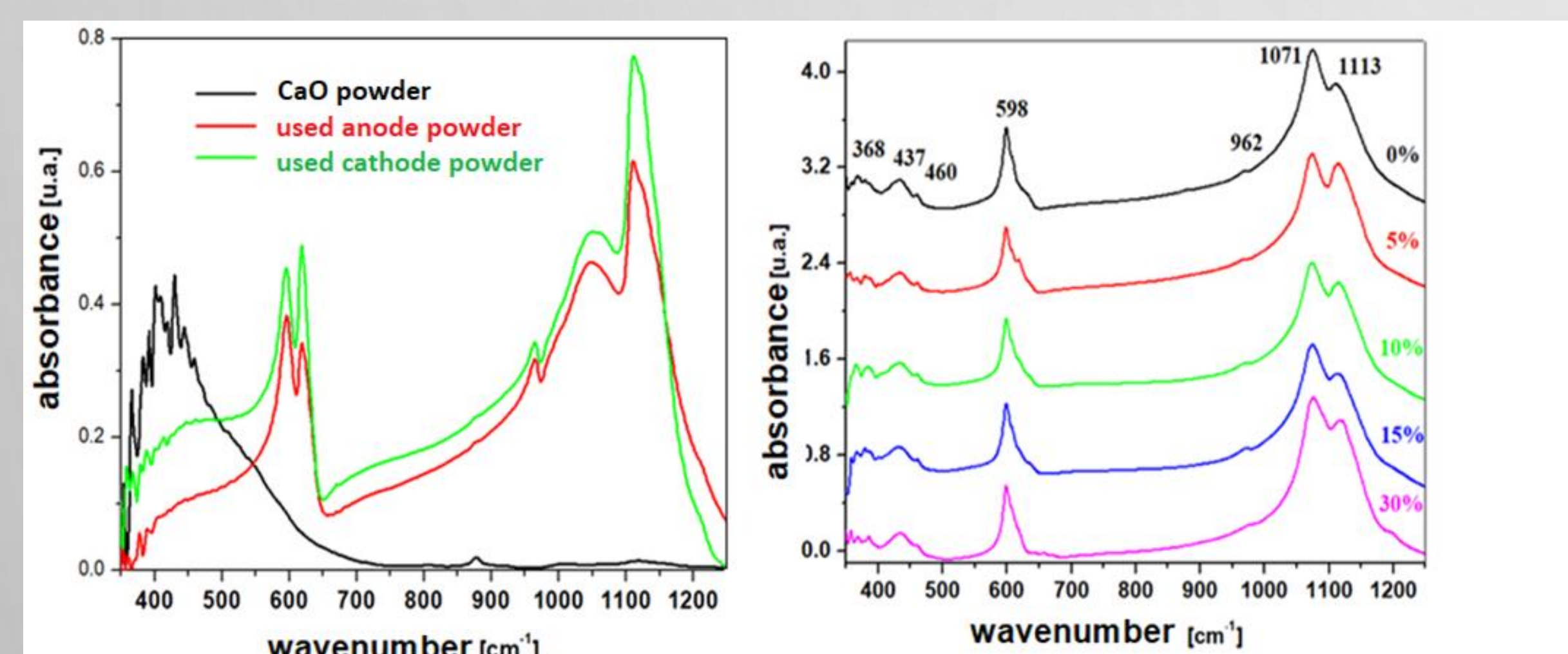


Fig. 2. FTIR spectra of recycled vitreous systems in the $x\text{CaO} \cdot (100-x)[4\text{PbO}_2 \cdot \text{Pb}]$ composition where $x = 0 - 30$ mol% CaO

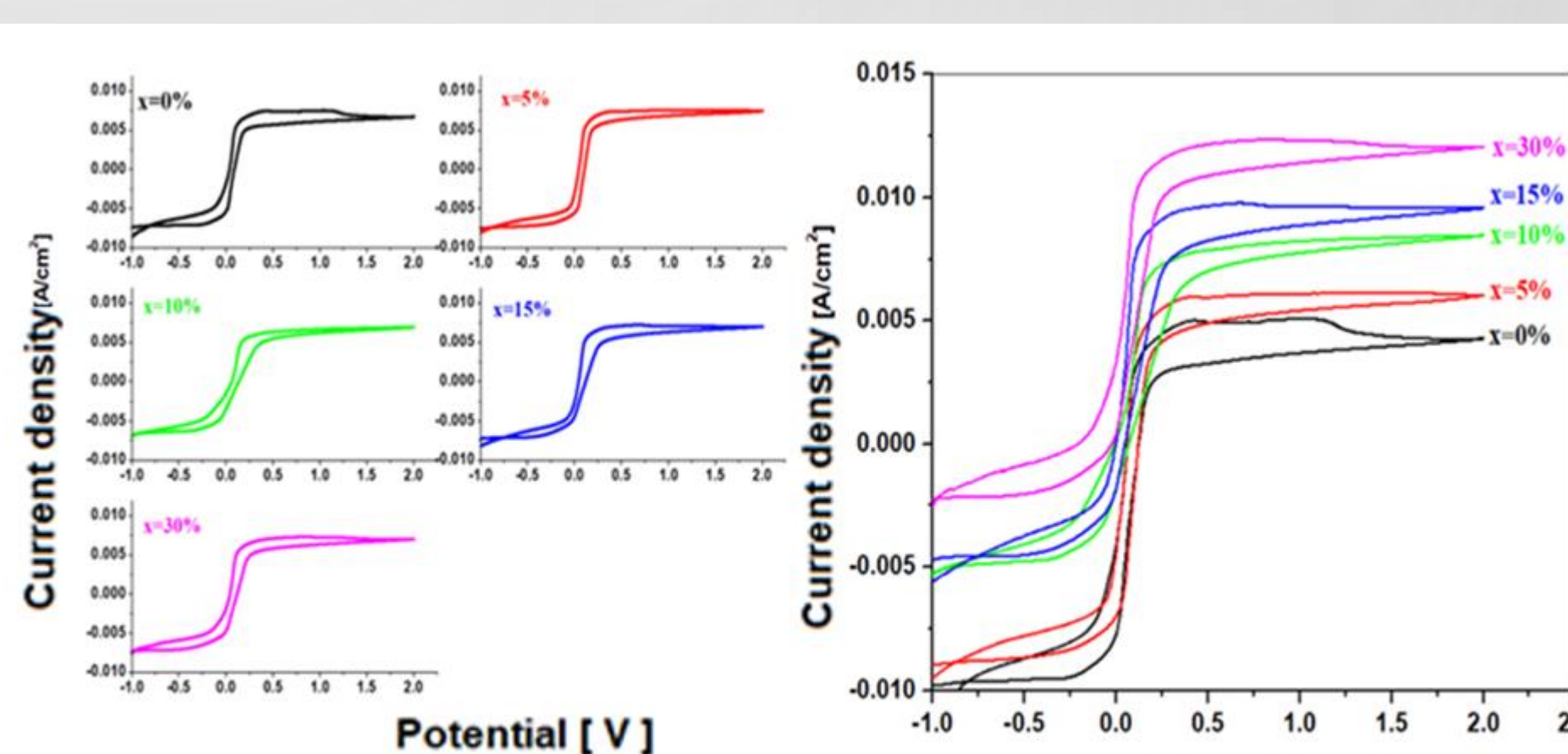


Fig. 4. Cyclic voltammograms of recycled vitreous systems in the $x\text{CaO} \cdot (100-x)[4\text{PbO}_2 \cdot \text{Pb}]$ composition where $x = 0 - 30$ mol% CaO

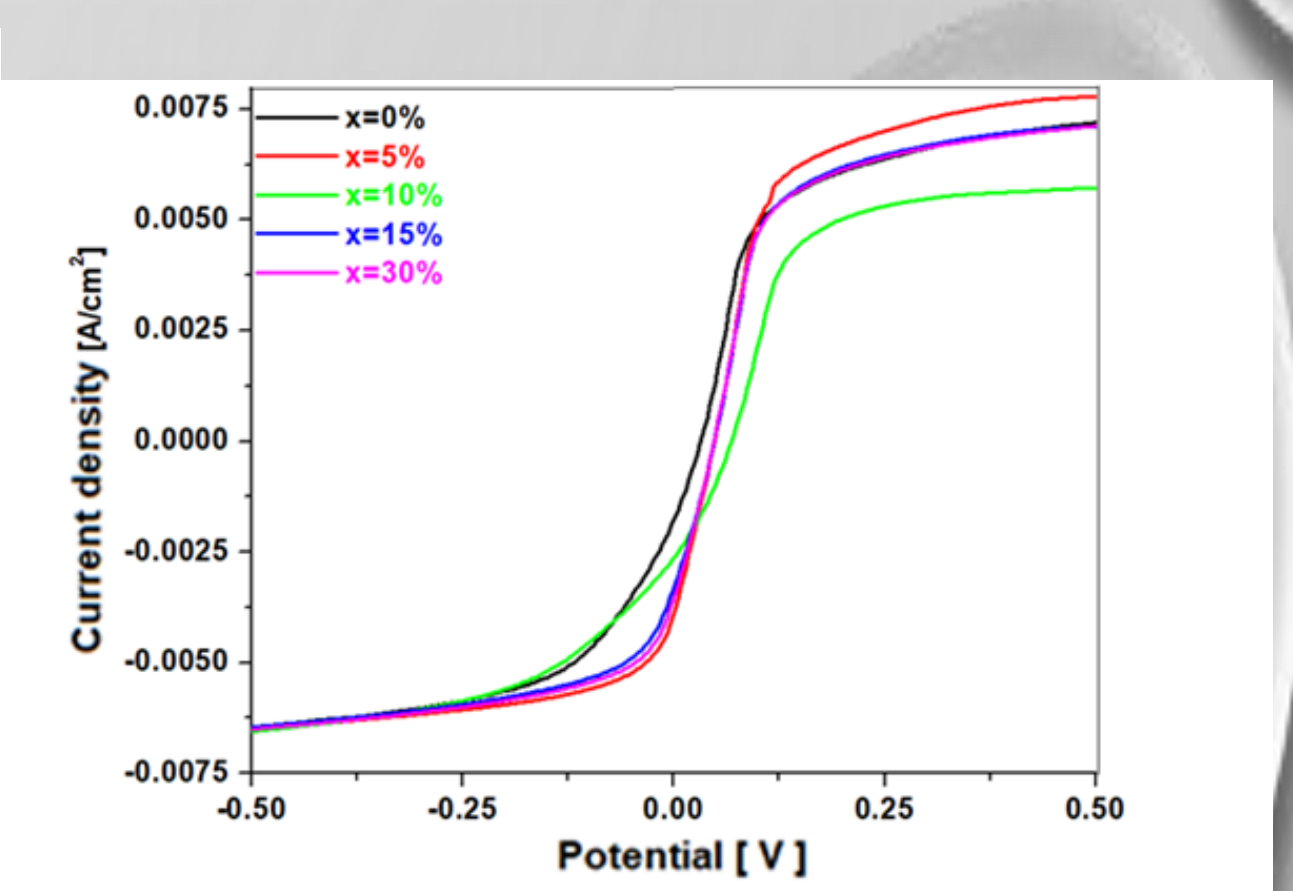


Fig. 6. Linear voltammograms of recycled vitreous systems in the $x\text{CaO} \cdot (100-x)[4\text{PbO}_2 \cdot \text{Pb}]$ composition where $x = 0 - 30$ mol% CaO

Conclusions

The general purpose of the own contribution chapters is to demonstrate the possibility recycling of anodic and cathodic plates from a used car battery and the possibility of optimization performance with other oxides through a cheap, eco-innovative and energy-efficient method for field of origin applications. The electrode materials were prepared investigated by physical methods of analysis (X-ray diffraction, IR spectroscopy, UV-Vis), optical (determination of optical gap energy) and electrochemical (cyclic voltammetry and linear voltammetry), in order to determine the structural, optical and conductive properties. In summary, the method presented in this dissertation, namely the method of subcooling melting has a major advantage compared to pyrometallurgical methods, namely that they do not occur emissions of sulfur oxides into the atmosphere at $1050\text{ }^\circ\text{C}$.

References

1. Simona Rada, Eugen Culea, Marius Rada, Petru Pașcuță, Spectroscopic methods of analysis, 2013, U.T. PRESS, Cluj -Napoca, pag. 117-153
2. Simona Rada, M. L. Unguresan, L. Bolundut, M. Rada, H. Vermesan, M. Pica, E. Culea, Structural and electrochemical investigations of the electrodes obtained by recycling of lead acid batteries, J. Electroanalytical Chemistry, 187
3. C.S. Martinez-Cisneros, A. Fernandez, C. Antonelli, B. Levenfeld, A. Varez, K. Vezzù, V. Di Noto, J.-Y. Sanchez, Opening the door to liquid-free polymer electrolytes for calcium batteries, Volume 353, 1 September 2020, 136525
4. S. Rada, L. Rus, M. Rada, E. Culea, N.Aldea, S. Stan, R. C. Suci, A. Bot, Synthesis, structure, optical and electrochemical properties of the lead sulfate-lead dioxide-lead glasses and vitroc ceramics, Solid State Ionics, Volume 274, June 2015, Pg 111-118