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Synthesis and Characterization of Phosphorus Based Ceramics For Positive Electrode: NPK Fertilizers Use As Phosphorus Precursor

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Introduction:

Historically, the LiCoO2 is the most used as active material for battery positive electrode because of its great potential (3.7-4.2 V), its interesting specific capacity (150 mA.h.g^{-1}) and its excellent life cycle [1].

However, the cobalt toxicity, its cost and its structural instability oriented research towards new materials more stable that can replace it. In other contexts, such as hybrid and/or electrical vehicles and transport tools (computers and mobile phones ...) have increased the scientific and technological research for new materials capable of storing energy and return through a system called accumulator. And research has identified the phosphate olive structure as the most prolific ceramic material for positive electrode.

LiFePO4 is a promising cathode material for Lithium-ion batteries. It provides high thermal stability and is synthesized using low cost materials.

Unfortunately LiFePO4 suffers from a low electrical conductivity, which is harmful to its electrochemical performance. Decreasing the particle size, coating the particles with carbon or doping with metal atoms can increase the conductivity of the material.

In this paper, we present the synthesis, physico-chemical and electrical characterization of lithium and iron doped Al-phosphorus-based ceramic. The NPK Fertiliser was used as Al and phosphorus precursors. The powder XRD spectrum shows a possible presence of $LiFePO_4$ and $Fe_2(PO)_3$ in the structure.

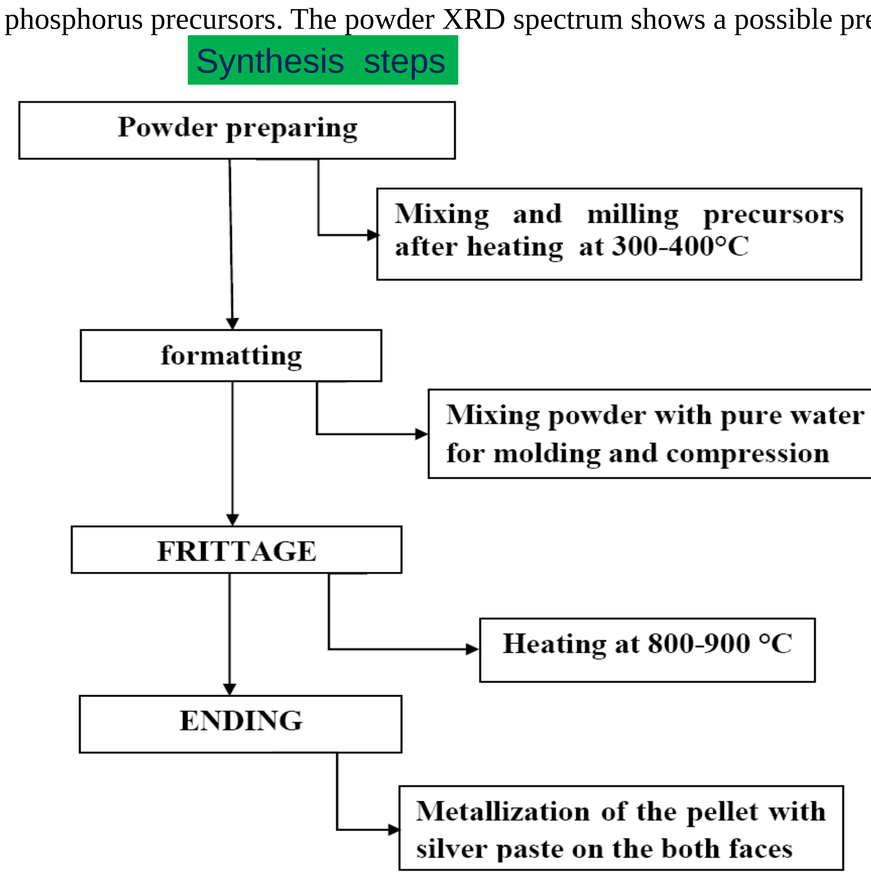

Fig.1: Heating furnace

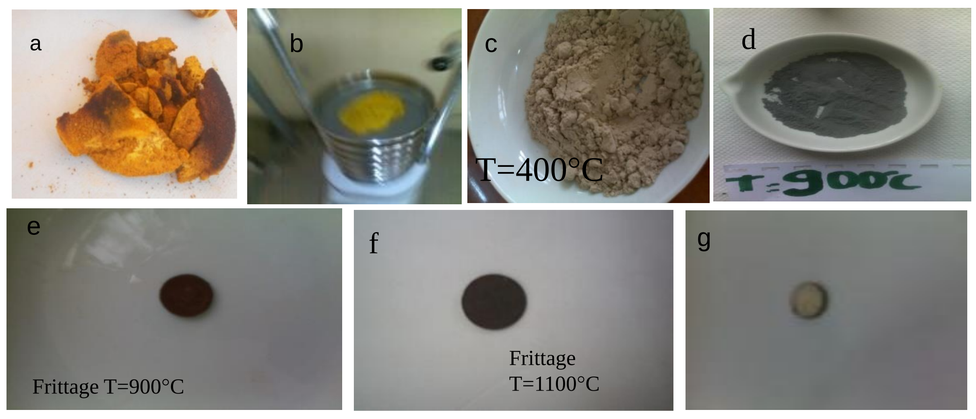

Fig.2: Synthesized ceramic products before and after final heating

a) Clusters obtained after heating at 400°C,
b) Sieving ceramic powder ,
c & d) Ceramic powder heated at different temperature,
e & f) Ceramic pellet,
g) Ceramic pellet after metallization with silver paste

The solid-state synthesis used here leads to large particle size materials due to an extended exposure of the sample to elevated temperatures which leads to an annealing process (fig 2.a). Hence, a melting process was performed on the obtained materials to reduce the particle size (fig 2.c). This should result in superior performance of sample for physics measurements. In fact, ceramic pellets obtained from the sample is more dense and present less failure between ceramic grains. Fig 3 shows grains distribution histogram issued from the particles size study after sieving. Even if the particles size is not more finer, more than half of the sample grains is in the range of 45 to 250 µm in size. That permits to obtain dense ceramic pellets observed in fig 2.e. For physical analysis, this ceramic pellets were metalized (fig 2.g) by serigraphy method. This method consist to lay a thin layer of silver paste on the area of the both faces separated by the ceramic pellet thickness.

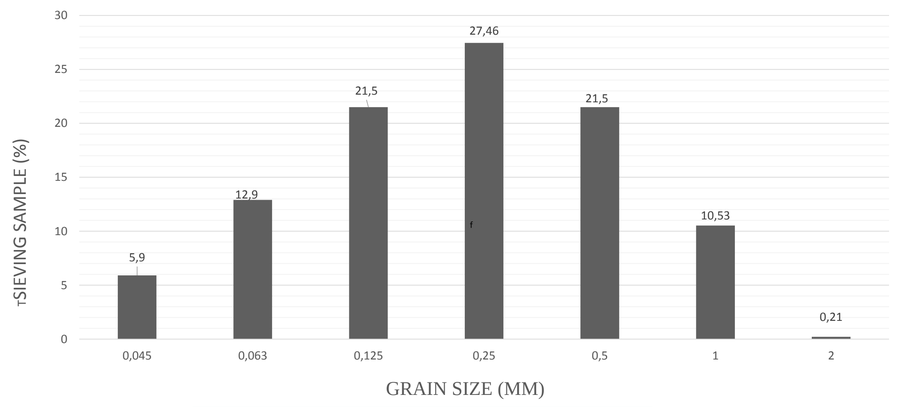

Fig.3: Distribution of grain size

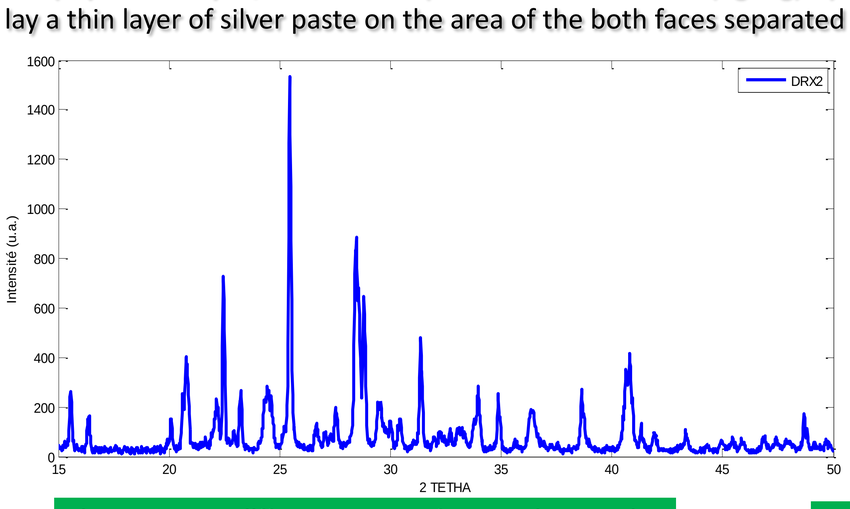

Fig. 4: X-ray diffractogram of ceramic powder

Fig. 5: thermal dilatation of the synthesized ceramic

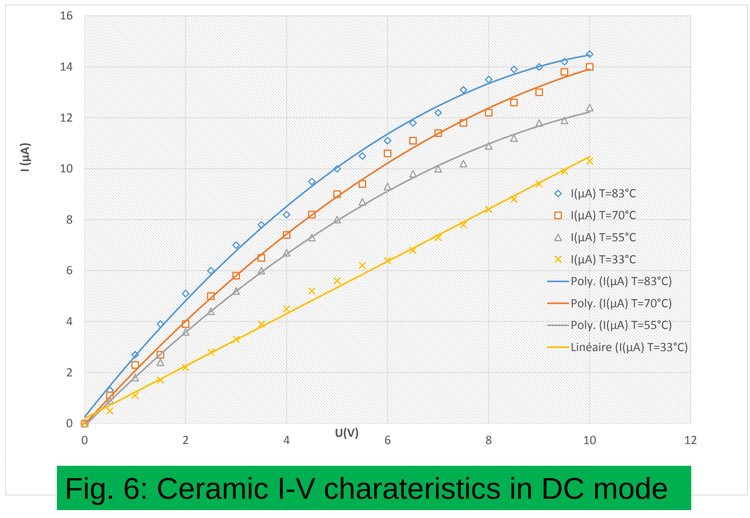

Fig. 6: Ceramic I-V charateristics in DC mode

table 1: electrical Constants at different temperatures (10^{-6})

T (°C)	α	β	γ	Re (Ω)	σ (S.cm^{-1})
33		1,027	0,203	9,74.10^5	1,30.10^{-7}
55	-0,0759	1,9917	-0,1035	5,02.10^5	2,54.10^{-7}
70	-0,0786	2,1802	-0,0348	4,60.10^5	2,77.10^{-7}
83	-0,1076	2,4965	0,2548	4,00.10^5	3,18.10^{-7}

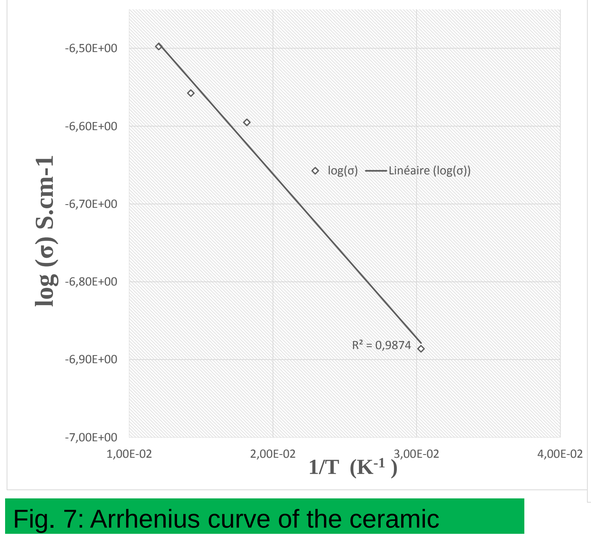

Fig. 7: Arrhenius curve of the ceramic

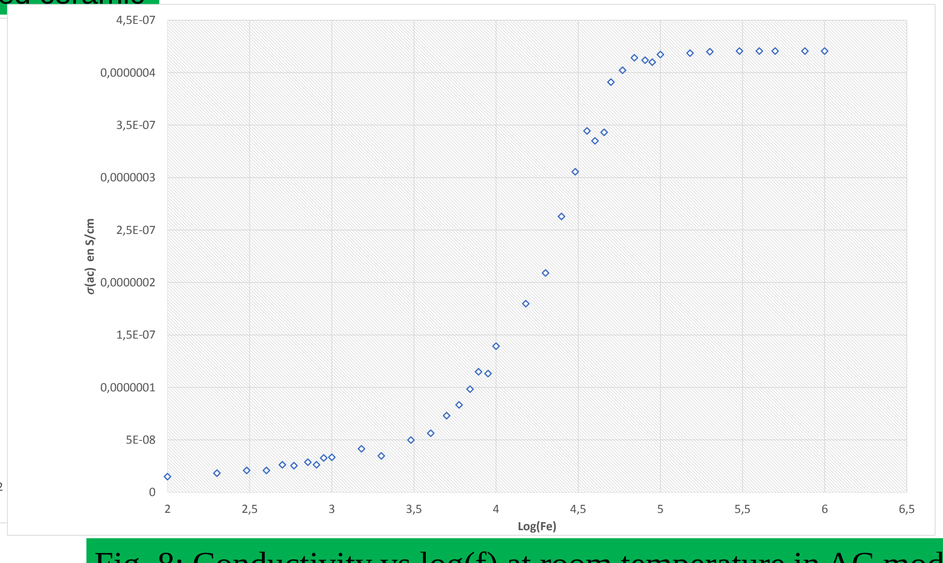

Fig. 8: Conductivity vs log(f) at room temperature in AC mode

Conclusion:

Structural analysis as X-ray spectrum (fig. 4) shows a possible presence of $LiFePO_4$ and $FePO_4$ in the heterostructure. However, some impurities are also found in this heterogeneous material. Study of the dilatation of material during elevated temperatures shows the stages changes when temperature increased. Moreover cristallisation phase is obtained when temperature is about 850°C, where glassy transition is observed (fig. 5). This hypothesis is confirmed by the results of the sample heated at 900°C showed at fig. 2.d.

Electrics analysis were realized by using curent-voltage measurement at DC mode (fig. 6). This easier technic permits to determine ohmic behaviour of ceramic material. Study of this electric parameter gives a value of the electric conductivity at room temperature about 1,30.10^{-7} S.cm^{-1}. This value is more important than intrinsic $LiFePO_4$ material conductivity (10^{-9} S.cm^{-1})[2]. Furthermore, Arrhenius curve analysis gives activation energy of the elaborated material. And the activation energy issue of the fitting Arrhenius curve is about 0,073 eV less than the intrinsic $LiFePO_4$ value given in literature. Electrical study of the second sample fig. 8 shows also two kinds of conductors as electron and ion in some range of frequency of alternative current. Two activations energy is found and its in order of 0,13 eV in low frequency and 0,035 eV at high frequency. Nevertheless its conductivity in low frequency is order to the first one and its value gives 1,50.10^{-8} S.cm^{-1}.

References

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Acknowledgments :

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