**Phase I** - 31.12.2015

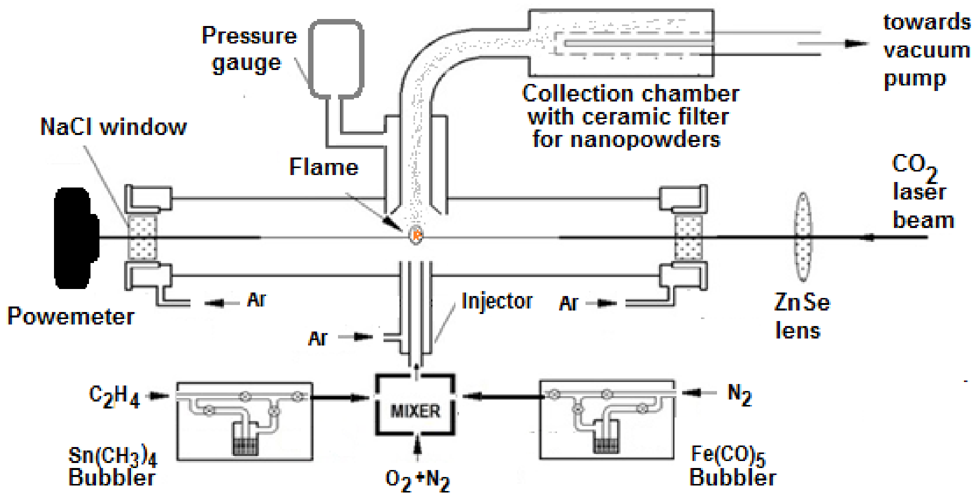
ABSTRACT OF SCIENTIFIC REPORT

**Synthesis, characterization and testing as anodes for Li-ion batteries of binary nanocomposites based on SnOx-$Fe_2O_3$**

Tin oxide is an attractive material that could substitute the currently used graphite as anode in lithium ion batteries (LIBs). $SnO_2$ has a theoretical capacity of 783 mA h $g^{-1}$ that is more than twice the value of graphite (372 mA h $g^{-1}$). Regarding the lithiation mechanism it is generally accepted that tin oxides undergo a first irreversible reduction with $Li^+$ions that allows nanoparticulate Sn particles to be formed finely dispersed into a $Li_2O$ matrix. The following lithiation processes involve reversible alloying of the Sn nanoparticles with Li, buffered against the volume change by the surrounding matrix of lithium oxide. The problems that arise when using Sn oxides as anodes in LIBs are the large irreversible capacity in the first cycle due to the $Li_2O$ formation, degradation of the oxide matrix during cycling and the tendency of Sn nanoparticles to aggregate into larger particles.

However, the practical use of $SnO_2$as negative electrode for LIBs is challenged by other two major issues. One of them is the poor cyclability because of the severe volume expansion and contraction (more than 200%) during the alloying-dealloying of the Sn nanoparticles with $Li^+$ion sthat leads to cracking and loss of electrical contact between the active material particles.

For the laser pyrolysis experiments we used a cw $CO_2$ laser ($\lambda$=10,6 μm) with 100 W maximum power; as metal prexcursors we employed $Fe(CO)_5$ and $Sn(CH_3)_4$, $O_2/N_2$ mixtures as oxidant and C2H4 as sensitizer

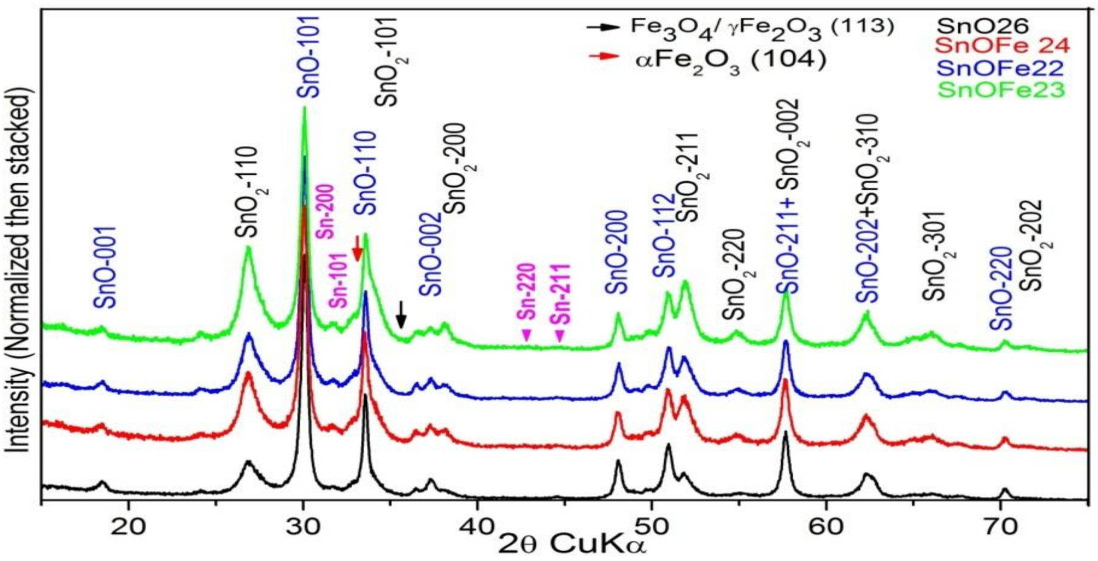



*Laser pyrolysis installation for the synthesis of Fe doped SnOx nanopowders*

**Table 1** Experimental parameters for the synthseis of tin oxide doped with Fe for the optimization of Sn/Fe/O composition for şi Li-ion reacargeable battery anodes

| Proba | $\phi C_2H_4 \rightarrow SnMe_4$ [sccm] | $\phi SnMe_4$ [sccm] | $\phi O_2$ [sccm] | $\phi N_2$ [sccm] → | | $\phi Fe(CO)_5$ [sccm] | Yield [g/h] |
|---|---|---|---|---|---|---|---|
| | | | | central | $Fe(CO)_5$ | | |
| **SnO26** | **15** | **15** | **10** | **10** | **-** | **-** | **0.55** |
| **SnO27** | **15** | **15** | **16** | **8** | **-** | | **0.54** |
| **SnO28** | **15** | **15** | **27** | **18** | **-** | | **0.73** |
| **SnOFe22** | **15** | **15** | **10** | **9.50** | **0.50** | **0.06** | **0.50** |
| **SnOFe23** | **15** | **15** | **10** | **9** | **1** | **0.12** | **0.45** |
| **SnOFe24** | **15** | **15** | **10** | **9.75** | **0.25** | **0.03** | **0.40** |
| **SnOFe25** | **15** | **15** | **10** | **9.62** | **0.38** | **0.05** | **0.40** |

Three undoped samples and other iron-doped samples were obtained (table1). The amount of oxygen in the undoped samples was varied to change the degree of tin oxidation translated in various SnO to $SnO_2$ ratios The Fe-doped samples were obtained using as reference the SnO26 sample synthesis conditions using increasing flows of iron precusor from SnOFe24, to SnOFe25, SnOFe22 and SnOFe23 where the highest flow of $Fe(CO)_5$ (1 sccm) resulted.



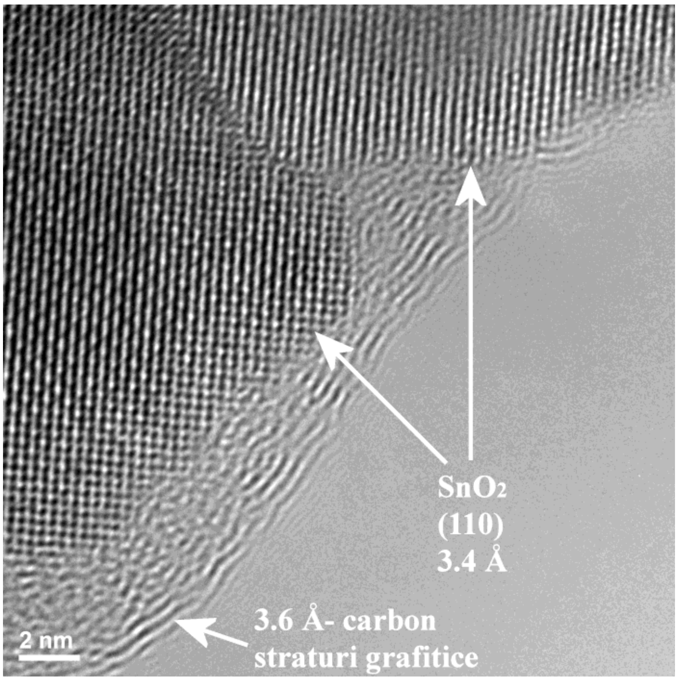

*XRD analyses fot the iron doped tin oxide samples*

Elemental composition evaluation (left) from EDAX and XRD characterisation of the two tin oxides: SnO and $SnO_2$ : most intense peak intensitiy ratio, mean crystallite size (right).

| Proba | EDAX [at%] | | | | *XRD* | | |
|---|---|---|---|---|---|---|---|
| | Sn | O | C | Fe | $I_{SnO2}/I_{SnO}$ | $D_{SnO2}$ *[nm]* | $D_{SnO2}$ *[nm]* |
| **SnO26** | 34.00 | 49.34 | 16.66 | | *0.16* | *7.1* | *18.8* |
| **SnO27** | 33.21 | 51.45 | 15.72 | | *0.42* | *8.3* | *14.1* |
| **SnO28** | 32.63 | 52.91 | 14.46 | | *0.94* | *10.7* | *20.0* |
| **SnOFe22** | 33.39 | 53.59 | 12.24 | 0.78 | *0.27* | *7.30* | *18.30* |
| **SnOFe23** | 31.69 | 52.60 | 13.36 | 2.35 | *0.43* | *8.00* | *17.70* |
| **SnOFe24** | 33.48 | 51.74 | 13.31 | 1.47 | *0.32* | *7.60* | *17.80* |
| **SnOFe25** | 35.25 | 51.32 | 12.53 | 0.90 | | | |

As can be seen from table 2, higher iron pentacarbonyl flow in the reaction zone is translated in higher dopant concentration, up to 2.35 atomic % in tin oxide-based powder. Comparing the introduced tetramethyltin flow and the quantity of tin-based powder resulted by laser pyrolysis, the tin conversion degree from vapor to solid phase is quite low, around 9% for SnO26 reference sample. Also, the Sn-Fe ratio in the precursor is around 9 times higher in the precursors than in the resulted SnOFe3 sample, due to much higher conversion of $Fe(CO)_5$ towards those of $Sn(CH_3)_4$ molecules in the laser oxidative pyrolysis conditions

*High resolution TEM image of SnOFe25 nanopowder*

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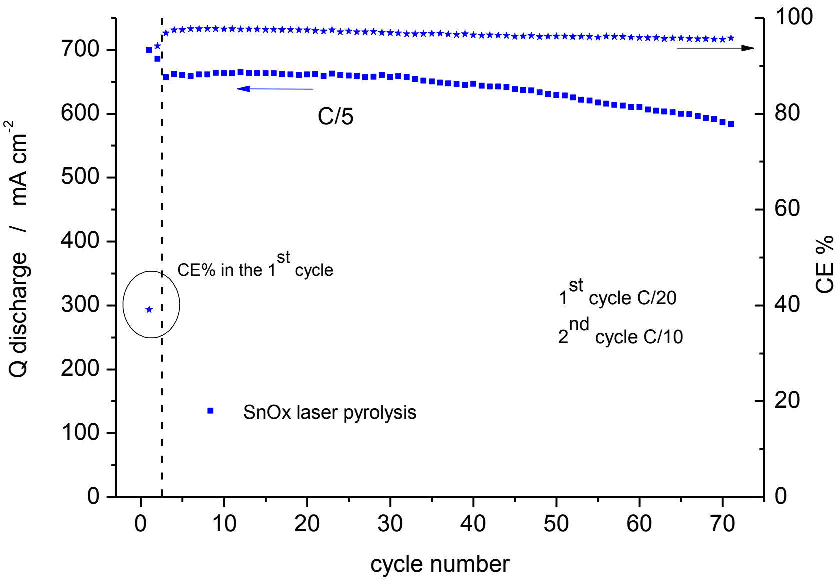
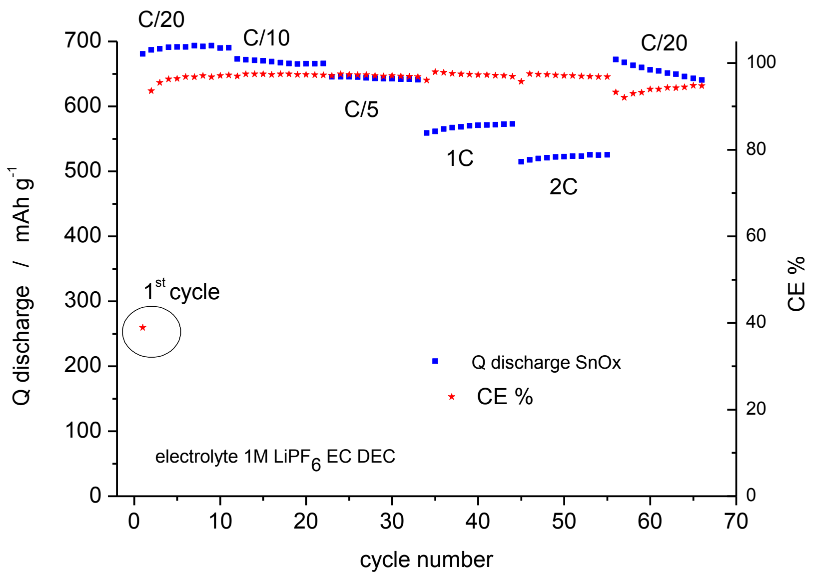



*Charge-discharge cycling test in Li-ion batteries anodes*




*Galvanostatic tests at different loading rates in Li-ion battery anodes*

As material for Li-ion batteries anodes , the galvanostatic test of charge/discharge and also those with rapid charging for a high number of cycles , our Tin-oxide based nanomaterials have a high performances in energy storage accompanied also by a good stability during cycling