Supplementary Information

Unveiling the stability of Sn/Si/graphite composites for Li-ion storage by physical, electrochemical and computational tools

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4) Instituto de Investigación en Físico Química de Córdoba, INFIQC, CONICET. Medina Allende s/n, Ciudad Universitaria, (X5016LAE) Córdoba, Argentina.
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1. DFT calculations

1.1. Thermodynamical stability and NMR chemical shift calculations

The DFT calculated free energy of formation (ΔG^0) was used to study the Li-Sn alloys stability. For a given structure the energy is calculated as:

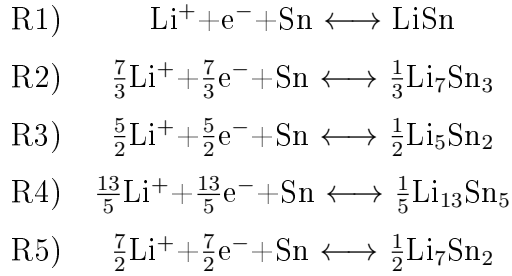$$\Delta G^0 = E_{Li_x Sn/Si_y} - x E_{Li_{bulk}} - y E_{Sn/Si_{bulk}}. \tag{1}$$

Where $E_{Li_{bulk}}$ and $E_{Sn/Si_{bulk}}$ are the energy per atom in the bulk metals and $E_{Li_x Sn/Si_y}$ is the alloy energy.

Table 1S shows the results of ΔG^0 corresponding to the different $Li_x Sn_y$ phases. From these values, we can get the equilibrium potential for the formation of the different alloys by setting $\Delta G^0 = -nFE_0$, where F is the Faraday constant and n is the number of electrons transferred.

To analyze the relative stability of the different alloys at different potentials, it is useful to write the alloying equations per Sn mol:

Table 1S: Formation energy calculated for different Li-Sn alloys using Equation 1 and equilibrium potential E_0.

Phase	ΔG^0 [eV]	$\Delta G^0/n_{Sn}$ [eV]	E_0 [V]
LiSn	-0.72	-0.72	0.724
Li_7Sn_3	-4.24	-1.41	0.605
Li_5Sn_2	-2.99	-1.50	0.598
$Li_{13}Sn_5$	-7.78	-1.54	0.597
Li_7Sn_2	-3.60	-1.80	0.514

$$\text{R1)} \qquad \text{Li}^+ + \text{e}^- + \text{Sn} \longleftrightarrow \text{LiSn}$$

$$\text{R2)} \qquad \tfrac{7}{3}\text{Li}^+ + \tfrac{7}{3}\text{e}^- + \text{Sn} \longleftrightarrow \tfrac{1}{3}\text{Li}_7\text{Sn}_3$$

$$\text{R3)} \qquad \tfrac{5}{2}\text{Li}^+ + \tfrac{5}{2}\text{e}^- + \text{Sn} \longleftrightarrow \tfrac{1}{2}\text{Li}_5\text{Sn}_2$$

$$\text{R4)} \qquad \tfrac{13}{5}\text{Li}^+ + \tfrac{13}{5}\text{e}^- + \text{Sn} \longleftrightarrow \tfrac{1}{5}\text{Li}_{13}\text{Sn}_5$$

$$\text{R5)} \qquad \tfrac{7}{2}\text{Li}^+ + \tfrac{7}{2}\text{e}^- + \text{Sn} \longleftrightarrow \tfrac{1}{2}\text{Li}_7\text{Sn}_2$$

The change of the free energy of each reaction gives the spontaneity criterion for the reaction of a mol of Sn with different amounts n_{Li^+} of Li^+ ions in solution, and n_e electrons in the working electrode. This reaction yields different lithiated species, say P_i, with the stochiometric coefficient n_i. Thus, in general we have:

$$\text{R6)} \quad n_{Li^+}\text{Li}^+ + n_e\text{e}^- + \text{Sn} \longleftrightarrow n_iP_i.$$
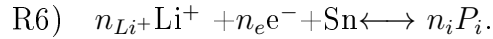
Using this notation, the free energy for any of the reactions R1-R5 can be written as:

$$\Delta G_i = n_i\mu_i - \mu_{Sn} - n_{Li^+}\tilde{\mu}_{Li^+}^S - n_e\tilde{\mu}_e^W, \tag{2}$$

where μ and $\tilde{\mu}$ denote the chemical and electrochemical potentials respectively. Thus, $\tilde{\mu}_e^W$ represents the electrochemical potential of electrons in the working electrode and $\tilde{\mu}_{Li^+}^S$ the electrochemical potential of Li^+ ions in solution. The last two terms are introduced in Equation 2 because electrons and Li^+ ions may flow into and out of the material being lithiated.

Assuming that the electrode potential is measured with respect to a pure Li reference electrode immersed in the same solution as the working electrode, taking into account that $n_{Li^+} = n_e$ and subtracting and adding a term $n_e\mu_{Li^0}$ (with μ_{Li^0} representing the chemical

potential of Li atoms in the pure lithium metal), we get:

$$\Delta G_i = n_i \mu_i - \mu_{Sn} - n_e \mu_{Li^0} + n_e \tilde{\mu}_e^R + n_{Li^+} \tilde{\mu}_{Li^+}^R$$
$$- n_{Li^+} \tilde{\mu}_{Li^+}^S - n_e \tilde{\mu}_e^W. \tag{3}$$

Where we used the fact that for the reference Li electrode $\mu_{Li^0} = \tilde{\mu}_e^R + \tilde{\mu}_{Li^+}^R$, been $\tilde{\mu}_{Li^+}^R$ and $\tilde{\mu}_{Li^+}^R$ the electrochemical potentials of electrons and core ions in the reference electrode, respectively. Since Li$^+$ ions are free to flow between the working and the reference electrode, we have $\tilde{\mu}_{Li^+}^R = \tilde{\mu}_{Li^+}^S$. Therefore , Equations 3 reduces to:

$$\Delta G_i = n_i \mu_i - \mu_{Sn} - n_e \mu_{Li^0} + n_e (\tilde{\mu}_e^R - \tilde{\mu}_e^W). \tag{4}$$

If we take into account that cell potential V_{cell} measured with respect to the metallic Li electrode is $V_{cell} = (\tilde{\mu}_e^R - \tilde{\mu}_e^W)/e_0$, where e_0 is the elemental charge, we get:

$$\Delta G_i = n_i \mu_i - \mu_{Sn} - n_e \mu_{Li^0} + e_0 n_e V_{cell}. \tag{5}$$

Equation 5 allows us to predict the stability of different alloys arising from the reaction of Li ions with Sn at a given electrode potential, according to reactions R1-R5. The term $n_i \mu_i - \mu_{Sn} - n_e \mu_{Li^0}$ is equal to ΔG^0, calculated previously with DFT, divided by the mols of Sn.

The same procedure was applied to the Li-Si alloys. Table 2S shows the values of ΔG^0, $\Delta G^0/n_{Si}$ and E$_0$.

Table 2S: Formation energy calculated for different Li-Si alloys using Equation 1 and equilibrium potential E$_0$.

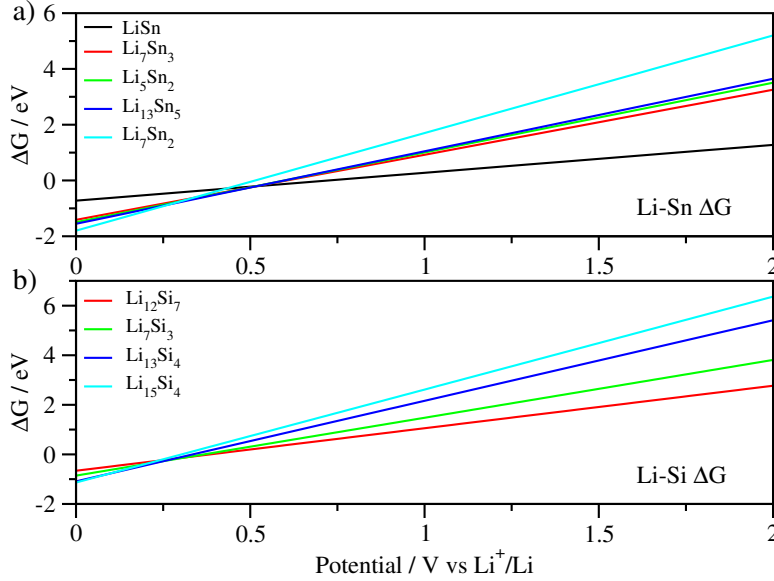| Phase	ΔG^0 [eV]	$\Delta G^0/n_{Si}$ [eV]	E$_0$ [V]
LiSi	-0.41	-0.41	0.410
Li$_{12}$Si$_7$	-4.62	-0.66	0.385
Li$_7$Si$_3$	-2.57	-0.86	0.367
Li$_{13}$Si$_4$	-4.35	-1.09	0.334
Li$_{13}$Si$_5$	-4.54	-0.91	0.349

Figure 1S: Free energy versus potential (Li^+/Li) corresponding to Li-Sn and Li-Si alloys.

1.2. GIPAW

Figure 2S shows the perfect correlation between the calculation an the experimnetal data. On one hand, the calculations for LiSn shows two resonances known to be related to the crystallographic sites 8e (42.5 ppm) and 4b (32 ppm) [1]. On the other hand, the results of calculations on the $Li_{13}Sn_5$ system also shows two resonances. The free fit of the experimental data gives a slope of -0.84 for LiSn and a slope of -0.922 for $Li_{13}Sn_5$, considering the unknown phase reported by Bekaert *et al* [1]. The proximity to -1 indicates a good correlation betwen experimental data and calculus.

Table 3S shows the experimental chemical shifts vs the theoretical ones, after the calculation of σ_{ref}. The values of δ_{iso}^{theo} coincide, to a good extent, with δ_{iso}^{exp}. In particular, the signal observed at $\delta_{iso}^{exp}=22$ ppm for the $Li_{13}Sn_5$ alloy phase [1] is predicted to occur at $\delta_{iso}^{theo}=21.8$ ppm. In our experiments the second signal associated to $Li_{13}Sn_5$ in the $Sn/\mu G$ 2:1 anode is observed at 21 ppm, very close to the predicted value.
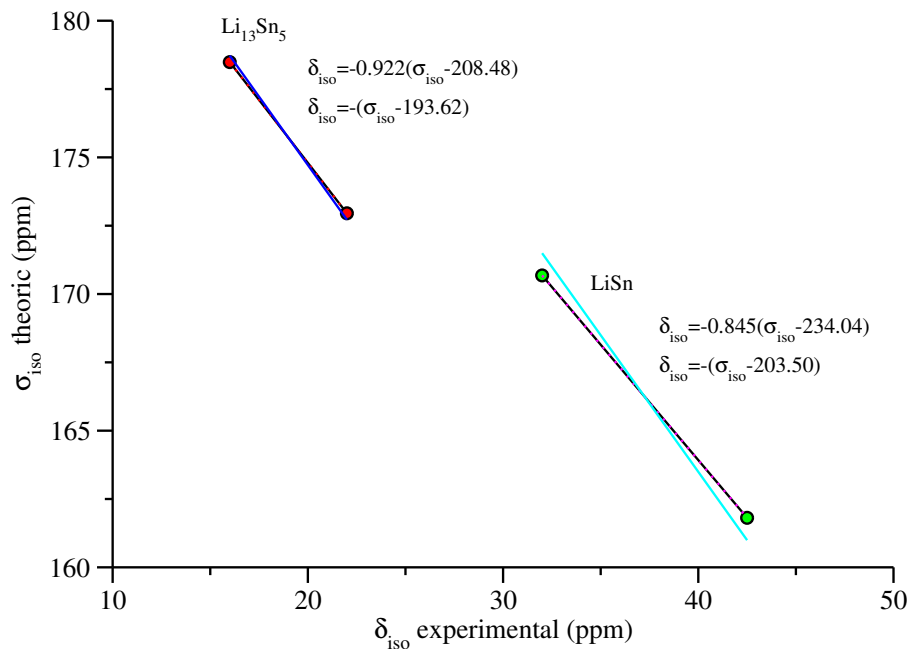
Figure 2S: Experimental isotropic chemical shift *vs.* theoretical isotropic chemical shielding calculated for different LiSn and $Li_{13}Sn_5$.

Table 3S: Experimental (from ref. [1])and theoretical chemical shifts of the LiSn and $Li_{13}Sn_5$ alloys.

Alloy	Experimental	Theoretical	
	δ_{iso}(ppm)	δ_{iso}(ppm)	σ_{iso}(ppm)
LiSn	32	32.8	170.7
	42.5	41.7	161.8
$Li_{13}Sn_5$	16.0	16.2	178.5
	22	21.8	173.0

[1] E. Bekaert, F. Robert, P. E. Lippens and M. Ménétrier, *J. Phys. Chem. C*, 2010, **114**, 6749–6754.

Table 4S: Theoretical capacity, Q_T, C-rate for the prepared anodes.

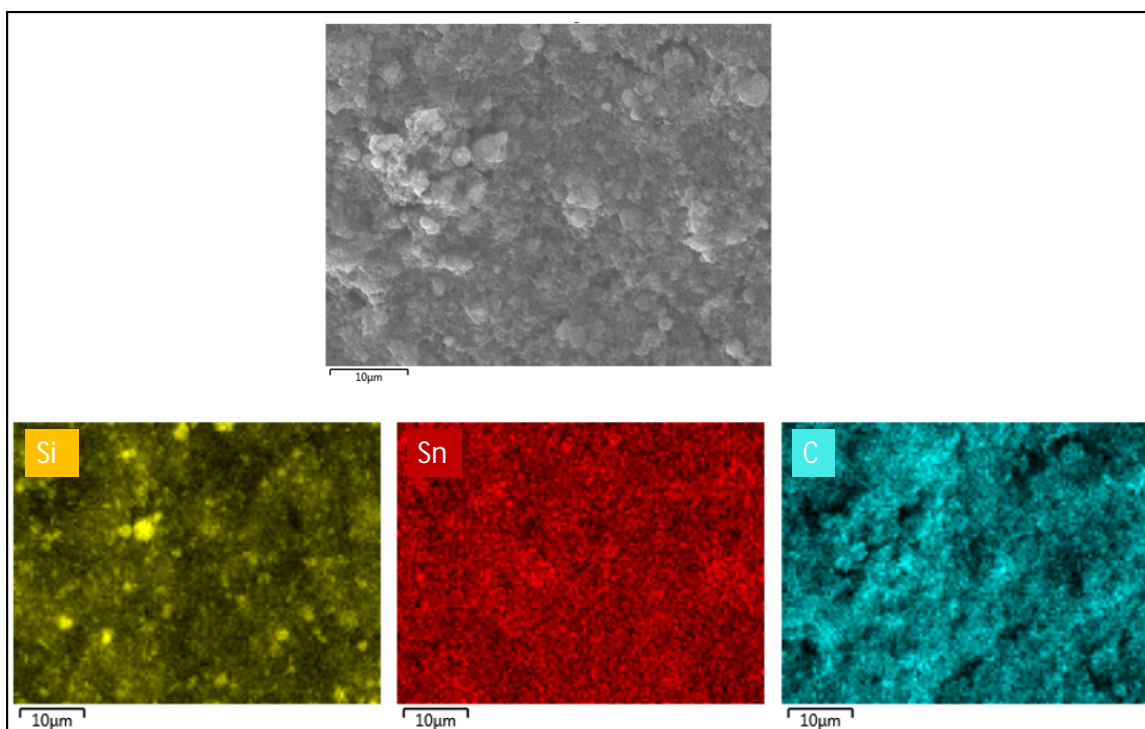| Anode	Q_T (mAhg^{-1})	C-rate
μG	372	C/4
Si/μG 2:1	2484	C/25
Sn/μG 2:1	781	C/8
Sn/Si/μG 1:1:1	1633	C/16

Figure 3S: SEM image and EDX analysis for the synthesized Sn/Si/μG powder.