SUPPLEMENTARY MATERIAL

Table S1. Loads (active material + binder) of the different working electrodes used in the galvanostatic cycling vs. Li/Li$^+$ experiments, in the potential ranges of 2.1 V – 3 mV (data in Table 1, Figures 1-3) and 0.9 V – *X* mV (*X* = lower cutoff voltage, LCOV, data in Figures 4-6) at 100 mA g^{-1}.

Electrode	Potential range	Load (mg)
80nSi/10BCNF27*G	2.1 V - 3 mV	1.10
60nSi/30BCNF27*G	2.1 V - 3 mV	2.90
45nSi/45BCNF27*G	2.1 V - 3 mV	2.50
30nSi/60BCNF27*G	2.1 V - 3 mV	3.40
10nSi/80BCNF27*G	2.1 V - 3 mV	2.80
80nSi/10BCNF27*A	2.1 V - 3 mV	3.00
60nSi/30BCNF27*A	2.1 V - 3 mV	1.20
45nSi/45BCNF27*A	2.1 V - 3 mV	0.60
30nSi/60BCNF27*A	2.1 V - 3 mV	2.30
10nSi/80BCNF27*A	2.1 V - 3 mV	2.70
80nSi/10BCNF16A	2.1 V - 3 mV	0.60
60nSi/30BCNF16A	2.1 V - 3 mV	1.30
45nSi/45BCNF16A	2.1 V - 3 mV	2.20
30nSi/60BCNF16A	2.1 V - 3 mV	2.20
10nSi/80BCNF16A	2.1 V - 3 mV	2.00
nSi	2.1 V - 3 mV	3.15
45nSi/45PR24G	2.1 V - 3 mV	2.50
45nSi/45rGO	2.1 V - 3 mV	1.00
45nSi/45BCNF16A	0.9 V - 3 mV	1.60
45nSi/45BCNF16A	0.9 V - 20 mV	2.40
45nSi/45BCNF16A	0.9 V - 40 mV	2.60
45nSi/45BCNF16A	0.9 V - 60 mV	1.50
45nSi/45BCNF16A	0.9 V - 80 mV	0.90
45nSi/45BCNF16A[*]	0.9 V - 80 mV	2.50
45nSi/45BCNF16A	0.9 V - 100 mV	1.20
45nSi/45BCNF16A	0.9 V - 120 mV	3.20

[*] Current density: 200 mA g^{-1}

PRELIMINARY OPTIMIZATION STUDY

1. Optimization of type of silicon, binder and conductive additive

Micro-crystalline silicon (mSi) and nano-crystalline silicon (nSi) based working electrodes were firstly prepared and afterwards evaluated as anodes for LIBs following the methodology described in Materials and methods section of the publication. The biopolymers sodium carboxymethyl cellulose (NaCMC) and Xanthan gum (XG) were used as electrode binders (B) in Si:B percentage weight ratios of 80:20 and 90:10. The specific discharge capacity (C_{disc}) in the 1st, 10th, 20th and 30th cycles of these electrodes (generically designated as xmSi/yB or xnSi/yB in which x and y are, respectively the weights percentages of mSi or nSi and binder) that were determined from the galvanostatic cycling vs. Li/Li$^+$ at an electric current density of 37.2 mA g^{-1} in the 2.1 V – 3 mV are shown in Figure S1. Regardless of Si:B ratio and silicon type, the use of the NaCMC leads to higher discharge capacities in the 1st cycle, especially from those electrodes with a 20 wt.% of this binder . The very high viscosity of XG binder aqueous solutions (100 times > NaCMC binder) should account for this capacity difference since it may causes an increase of the resistance to the Li$^+$ migration through the electrode active material. Nevertheless, as it can be seen in Figure S1 only the nSi based electrodes are able to retain some capacity along cycling.

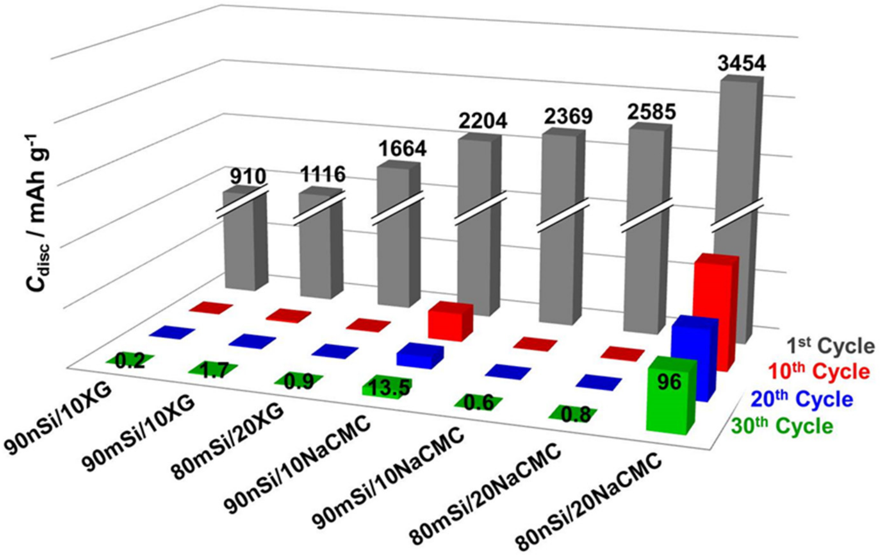

Figure S1. Specific discharge capacity in the 1st, 10th, 20th and 30th cycles from the galvanostatic cycling of different micro-silicon (*x*mSi/yB) and nano-silicon (*x*nSi/*y*B) based electrodes at an electric current density of 37.2 mA g^{-1} in the 2.1 V – 3 mV potential range. B is the binder, namely sodium carboxymethyl cellulose (NaCMC) and Xanthan gum (XG), and *x* and *y* are the weight percentages of silicon and binder, respectively, in the electrode.

Following these experiments, new silicon electrodes containing a conductive additive (E) to improve their electrochemical properties were prepared by mixing, in a Retsh MM 400 Mixer Mill, 70 wt.% of nSi, 10 wt.% of E and 20 wt.% of the NaCMC in an aqueous solution at a concentration ca. 1 wt.% (see the experimental section of the publication). These electrodes were named as 70nSi/10E/20NaCMC, being the E additive a carbon black C65 (CB), a synthetic KS6 graphite (SG-KS6) or a biogas-derived graphitic nanofibers (BCNF27*G) with different electric conductivity and BET surface area (Table S2).

Table S2. Electric conductivity (σ) and BET surface area (S_{BET}) of the conductive additives (E).

E	σ / S cm^{-1}	S_{BET} / m^2 g^{-1}
CB	12	~ 80
BCNF27*G	65	~ 36
SG-KS6	145	< 10

The specific discharge capacity (C_{disc}) *versus* cycle number plots from the galvanostatic cycling at 37.2 mA g^{-1} in the 2.1 V – 3 mV potential range of 70nSi/10E/20NaCMC electrodes are reported in Figure S2. For comparison, that of 80nSi/20NaCMC electrode is included in the same figure. As expected, the use of an E additive increases the electrode capacity by favoring the electric conductivity between the active material particles and reducing the electrode polarization. Among them, those such as CB additive with higher specific surface area which could better contribute to accommodate the volume changes of the Si in the electrode lead to better results.

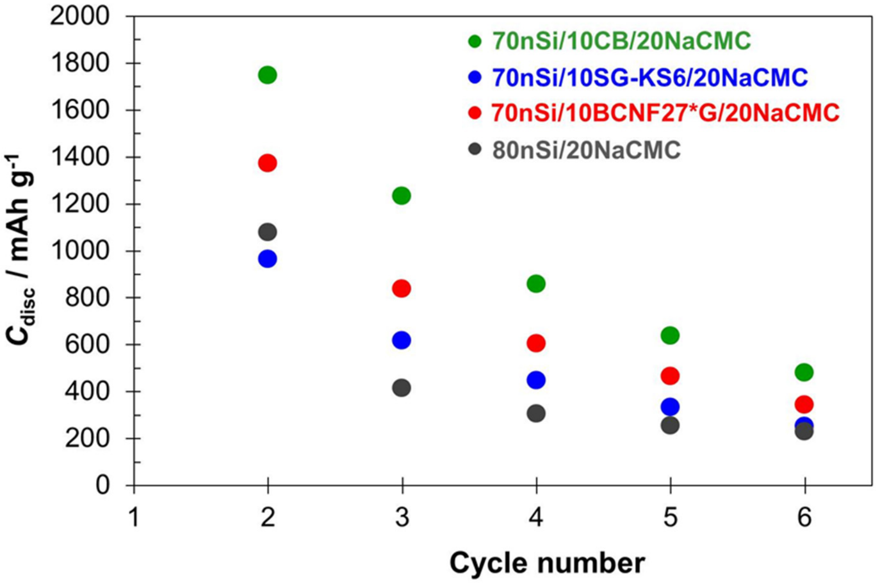

Figure S2. Specific discharge capacity against cycle number plots from the galvanostatic cycling of 70nSi/10E/20NaCMC electrodes (E: CB, SG-KS6 or BCNF27*G) and 80nSi/20NaCMC electrode at an electric current density of 37.2 mA g^{-1} in the 2.1 V – 3 mV potential range.

Therefore, from these results it can be concluded that the optimal option for the electrode composition as regards type of silicon, conductive additive and binder appears to be nSi (70 wt.%), CB (10 wt.%) and NaCMC (20 wt.%), respectively.

2. Optimization of the nSi/C composite preparation methodology

As mentioned in the experimental section of the publication, the nSi/C active composites, which included CB conductive additive, were prepared by three different procedures, namely Simple Addition (SA), Mechanical Milling (MM) and Dispersion in 2-propanol (DP) of the components. The purpose of these experiments was to set up a simple, quick, economical and scalable procedure. To this end, three nSi/C with the same composition (45 wt.% of nSi, 45 wt.% of BCNF16A carbon matrix, 10 wt.% of CB) were prepared by means SA, MM and DP methods. Afterwards, the corresponding working electrodes were obtained by mixing 80 wt.% of the active composite and 20 wt.% of NaCMC binder and their electrochemical performance as anodes was analyzed from a comparative point of view. Following the composite preparation, these electrodes of equal composition were named SA, MM and DP. The galvanostatic cycling results in Figure S3 evidences some differences among them as regards both specific capacity and capacity retention along cycling. Specifically, the capacity retention along cycling of DP electrode is much higher than those MM and SA electrodes, particularly from cycle 10, which indicates that the carbon material matrix is better accommodating the volume changes during *lithiation/delithiation* process. As a result, a discharge capacity of 525 mA g^{-1} was determined for DP electrode after 30 discharge-charge cycles against values of < 284 mAh g^{-1} for SA and only 115 mA g^{-1} for MM (Figure S3).

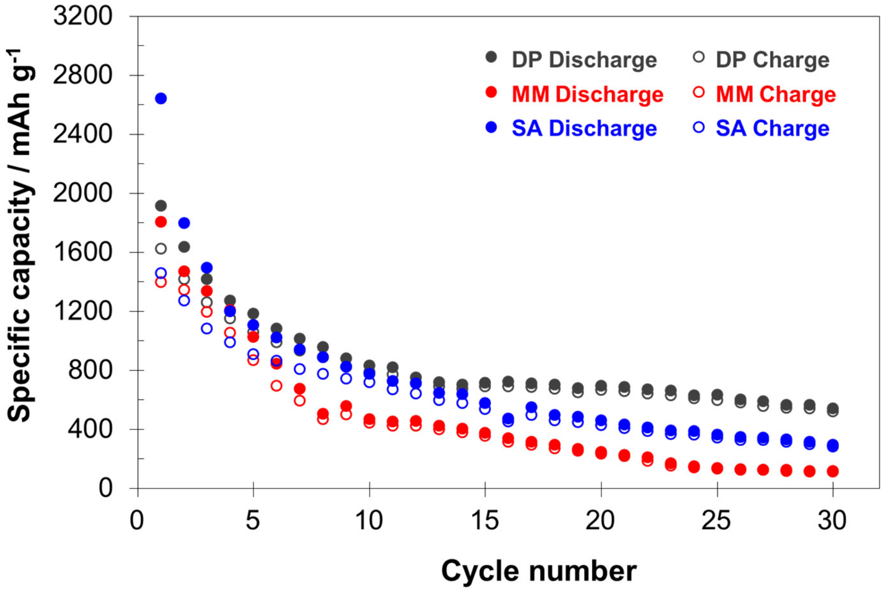

Figure S3. Specific capacity against cycle number plots from the galvanostatic cycling of DP, MM and SA electrodes at an electric current density of 100 mA g^{-1} in the 2.1 V – 3 mV potential range.

The different electrochemical results of SA, MM and DP electrodes can be explained on the basis of their analysis by SEM/EDX prior cycling as regards nSi/C components distribution (Figures S4, S5). Si and C are homogenously dispersed in DP electrode, thus facilitating the carbon matrix accommodation role during cycling and finally leading to a more stable electrode as seen in Figure S3. On the contrary, the carbon material and Si particles are forming separated agglomerates in SA electrode.

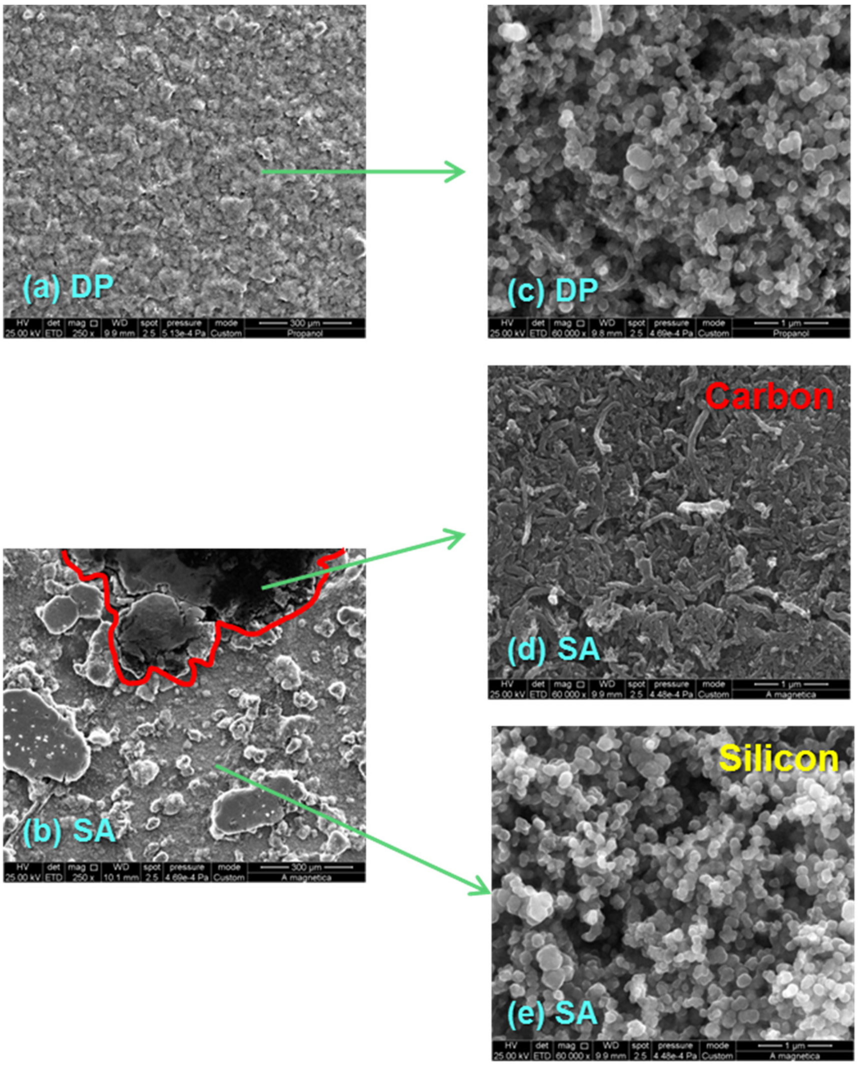

Figure S4. SEM images of DP electrode (a) 250x and (c) 60000x; and of SA electrode (b) 250x, (d) and (e) 60000x.

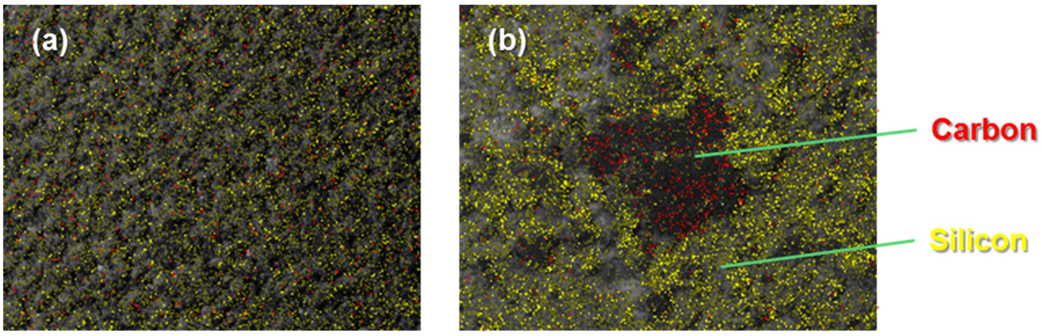

Figure S5. SEM/EDX images of (a) DP electrode and (b) SA electrode at 250x.

Therefore, it can be concluded that dispersing the active materials in 2-propanol is the most suitable method to mix them in a homogeneous way, allowing to get suitable electrodes to be cycled in LIBs.