Metal (Ni and Bi) coated porous silicon nanostructure, High-performance anode materials for lithium ion batteries with high capacity and stability

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Abstract

Herein, metal (nickel and bismuth) nanoparticles are supported on porous silicon flour (PSiF). Then they are proposed as high-performance anode materials for lithium ion battery. In this way, a facile procedure is introduced for the in-situ electroless assembling of nickel and bismuth nanoparticles on PSiF without using any reducing agent. The Metal@PSiF nanostructures with different Metal/Si ratio are prepared through the chemical reduction of the metals ions and oxidation of the surface of Si atoms, in a solution containing fluoride ions. The composition and morphological properties of the nanostructures are investigated using SEM, XRD, XPS and EDS. Also, galvanostatic charge-discharge and cyclic voltammetry are used to evaluate the electrochemical performance of the proposed anode materials. The synthesized Bi@PSiF nanostructure offers a specific capacity of 3245 mAh g⁻¹ at the 0.1 C rate while the Ni@PSiF shows a specific capacity of 2585 mAh g⁻¹ at the same C-rate. Both nanostructure still retains a specific capacity of about 2000 mAh g⁻¹ after 100 cycles, which is more than five-times larger when it compared with graphite (372 mAh g⁻¹). The obtained results confirm that the new nanostructures are an excellent candidate for anode material in advanced lithium-ion batteries with enhanced capacity and excellent columbic efficiency.

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1. Introduction

Li-ion batteries have been used in energy-storage applications, due to their superior charge storage properties (including high capacity and low self-discharge rates) in comparison with other rechargeable batteries [1]. However, to achieve super-high energy density, advanced electrode materials with high energy storage capacities must be developed to replace traditional LiCoO_2 cathode and graphite anode materials [2]. In the case of the anode, considering specific capacities in combination with such parameters as material abundance, cost, and toxicity, aluminum, tin, and silicon seem to be the most promising candidates to replace carbon anodes [3]. Among this electrode materials, silicon is far ahead regarding its gravimetric capacity that is approximately four times higher than capacities of aluminum and tin and about ten times greater than the capacities of traditional graphite anodes [3]. The unmatched combination of high capacity, attractive charge-discharge profile, silicon availability, low cost and environmental friendliness, makes silicon a very promising anode material. However, silicon still has not been implemented in commercial batteries due to its low electronic conductivity, slow lithium diffusion and the huge (up to 400 %) volume changes during cycling [4]. Recent studies on Si nanostructures such as nanowires [5-7], macro- [8-10] and nano-porous materials [11], nanocomposites [12,13], thin films [14,15], nanobelt [16] and nanotube [17] show significant promise in overcoming this issues since these types of nanostructures can provide individual geometries to accommodate the large volumetric expansion and facilitate the lithium ions insertion and extraction into the anode matrix, without mechanical fracture of active materials [18].

In this work, in an attempt to improve the electrochemical performance of silicon-based anodes, porous silicon was prepared by metal-assisted chemical etching of commercial silicon powder. Then, nickel and/or bismuth nanoparticles were deposited on the surface of porous silicon flour using a facile electroless approach. The electrochemical evaluations revealed that both of the anode materials (Ni@PSiF and Bi@PSiF) offer higher specific capacity as well as cyclic stability in Li-ion battery in comparison with commercial silicon powder and porous silicon flour.

2. Experimental

2.1. Preparation of PSiF

Metal-assisted chemical etching of silicon was done according to the literature [19]. Briefly, 5.0 g of polycrystalline Si powder (325 meshes) was dispersed in 100 mL of a solution, which consisted of HF (5 M) and AgNO₃ (5 mM). After mild stirring for about 10 min, the Ag nanoparticles were deposited on the surface of silicon microparticles. Then, the remaining Ag precursors were removed by rinsing three times with distilled water. After that, the Ag-coated silicon powder was dispersed in an etchant solution (100 mL) consisting of 5 M HF and 0.1 M hydrogen peroxide (H₂O₂) at 50 °C for 30 min, to synthesize Ag-coated PSiF. Finally, the Ag nanoparticles completely removed by immersing the Ag-coated PSiF in 5 M nitric acid for 2 h to obtain the PSiF.

2.2. Preparation of metal coated PSiF nanostructures

The detailed mechanism of the galvanic replacement of surface silicon atoms with noble metals has been described in the literature [20]. As can be seen in the following half-reactions, the elemental silicon can act as a reducing agent in the presence of fluoride ions [20]:

Where M denotes any metal (nobler than hydrogen such as copper, gold, bismuth, etc.). In the case of less noble metals such as nickel and cobalt, due to the fact that the redox potential of these metals is negative, hydrogen evolution dominates over the metal displacement. So, the fluoride-containing solution at pH 8 must be used for metal deposition on the silicon surface [21]. Based on the mentioned behavior of silicon in fluoride-containing solutions, we devise a facile wet electroless approach for the preparation of Ni@PSiF and Bi@PSiF nanostructures.

In the case of Bi@PSiF, 1.0 g of PSiF ultrasonically dispersed in 100 mL of HF (0.1 M) solution. Then, 100 mL of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ with different concentration (4.0, 5.0, 6.0 and 7.0 g/L) was added with vigorous stirring. After about 30 min, the obtaining nanostructures were washed three-time with water and dried at room temperature for 12 h. For the Ni@PSiF preparation, 1.0 g of PSiF was dispersed in a solution containing 0.1 M of ammonium fluoride (pH 8). After that, 100 mL of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ with different concentration (4.5, 9.0, 13.5 and 18.0 g/L) was added to the stirring mixture, drop by drop. After about 1 h, the resulting nanostructures were filtered and dried at room temperature.

2.3. Materials Characterization and Electrochemical Measurements

The morphology and size of the synthesized nanocomposites were investigated by a field emission scanning electron microscope (FE-SEM, Hitachi S4160, Tokyo, Japan) and a transmission electron microscope (Philips/FEI CM200 operating at 200 kV). To confirm the synthesis of the nanocomposites, a Bruker D₈/Advance X-ray diffractometer with Cu-K_α radiation ($\lambda = 1.5418 \text{ \AA}$) was used. The chemical composition of the nanocomposite was analyzed based on obtained EDS spectra (Philips XLS instrument, The

Netherlands) in ambient conditions. An X-ray photoelectron spectrometer (XPS), Model XR3 E2–(VG Microtech) with twin anode X-ray source was used for the XPS analysis. Electrochemical evaluations including cyclic voltammetry and galvanostatic charge-discharge tests were done using an Ivium potentiostat/galvanostat electrochemical analyzer (pocket STAT Model) with a homemade two electrode electrochemical cell (similar to Swagelok-type cells) between cut-off potentials of 0.01 and 1.50 V. A typical working electrode (anode) was prepared by hand mixing of 80 wt.% active material (silicon-based nanocomposites) with 10 wt.% PVDF binder and 10 wt.% acetylene black in N-methyl-2-pyrrolidone (NMP) to form a slurry. Then, the resulting slurry was uniformly pasted on Cu foil with a blade. Then it was dried at 120 °C under vacuum. The loading of each anode was usually around 2.5 mg cm⁻². Pure lithium foils were used as both the counter and reference electrodes. For separation of the anode and cathode, a polypropylene separator (Celgard) was used. The electrolyte was prepared from 1.0 M LiClO₄ in a mixture of DMC (dimethyl carbonate) and EC (ethylene carbonate) with 1:1 volume ratio. In galvanostatic charge-discharge experiments, C rates were calculated basing on the assumption that the material was composed of silicon only.

3. Results and discussion

3.1. Characterization of the Metal@PSiF nanostructures

The elemental analysis of the different nanostructures of Ni@PSiF and Bi@PSiF were carried out using the EDS technique. The results (Table 1 and 2) show that increasing the concentration of nickel or bismuth precursor's the solution cause increasing the metal content of Metal@PSiF nanostructures. Figs. 1A and 1B show the EDS spectra of Ni@PSiF (sample 3) and Bi@PSiF (sample 7) and their chemical compositions as well as their elemental mappings. The EDS spectra of Ni@PSiF demonstrates the presence of

silicon and nickel, while EDS spectra of Bi@PSiF confirms the presence of bismuth and silicon. The above results confirm that both nanostructures (with different metal/Si ratios) were successfully synthesized. **“Here Tables 1 & 2”**

Figs. 1C and 1D show the FE-SEM images of Ni@PSiF (sample 3) and Bi@PSiF (sample 7) nanostructures. As can be seen, the metal (Ni and Bi) nanoparticles have been uniformly supported on the surface of PSiF with the diameter range of 50 to 80 nm. The XRD patterns of Ni@PSiF and Bi@PSiF were also recorded over the 2θ ranges of $20-100^\circ$ (Fig. 2 A). The characteristics peaks of PSiF at 2θ of 28.4° , 47.2° , 56.2° , 69.1° , 76.5° , 88.2° and 94.8° which can be assigned to the planes of Si (111), Si (220), Si (311), Si (400), Si (331), Si (442) and Si (511), respectively [22] are presented in the XRD patterns PSiF (curve a), Ni@PSiF (curve b) and Bi@PSiF (curve c) nanostructures. Also, the XRD pattern of Ni@PSiF exhibited the peaks located at $2\theta = 44.7^\circ$, 52° , 76.4° , 93.1° , and 98.7° which are belong to the planes of (111), (200), (220), (311) and (222) FCC lattice structure of nickel nanoparticles [23]. Moreover, the XRD pattern of Bi@PSiF nanostructure showed the diffraction peaks at the 2θ of 27.2° , 38.1° , 39.7° , 48.8° , 62.2° , 64.7° , 70.1° , 72.2° and 85.7° , which is quite consisted with the literature XRD pattern of rhombohedral bismuth nanoparticles (JCPDS no. 05-0519) [24]. **The TEM images of Ni@PSiF (Fig. 2B) and Bi@PSiF (Fig. 2C) exhibit the efficient loading of Ni and Bi nanoparticles on the surface of PSiF. “Here Figures 1 & 2”**

X-ray photoelectron spectroscopy (XPS) analysis also confirms the formation of Ni@PSiF and Bi@PSiF anode materials. The wide scan XPS spectra for the both nanostructures are shown in Fig. 3A. As can be seen, Ni@PSiF and Bi@PSiF exhibit spine-orbit coupled doublets (Si $2p^{3/2}$ and Si $2p^{1/2}$) except for the binding energy of Si in the nanocomposites [25]. The high-resolution XPS spectra (Fig. 3B) indicates that these two peaks are located at 105.9 and 109.2 eV, respectively. Also, the Bi@PSiF XPS survey

exhibited two asymmetrical peaks at 166.1 and 171.7 corresponds to the spine-orbit split states of Bi $4f^{7/2}$ and $4f^{5/2}$ (Fig 3 D) while the Ni@PSiF XPS survey exhibited the characteristic peaks of Ni nanoparticles [26] “Here Figure 3”

Before metal coating, the Brunauer–Emmett–Teller (BET) technique was used for determination of the specific surface area of PSiF based on nitrogen adsorption-desorption isotherms. The obtained results revealed that the obtained PSiF delivers a specific surface area up to $38.93 \text{ m}^2 \text{ g}^{-1}$, in comparison with that of the as-received nonporous Si microparticles ($1.04 \text{ m}^2 \text{ g}^{-1}$), which confirm the porous structure formation during the etching process in PSiF. The nitrogen adsorption-desorption isotherms of Ni@PSiF (sample 3) and Bi@PSiF (sample 7) were also investigated. The higher specific surface area of the Ni@PSiF ($47.17 \text{ m}^2 \text{ g}^{-1}$) and Bi@PSiF ($51.36 \text{ m}^2 \text{ g}^{-1}$) in comparison with PSiF ($38.93 \text{ m}^2 \text{ g}^{-1}$) indicates the efficient loading of metal nanoparticles on the surface of PSiF.

3.2. Electrochemical performance of Metal@PSiF nanostructures

First of all, the cyclic voltammograms of different silicon-based anodes were performed at 0.01 - 1.50 V vs. Li/Li⁺ as a potential range with a scan rate of 0.1 mV/s. The obtained results (Fig. 4) revealed that the shapes of the voltammograms are consistent with the previously reported results by other researchers for nanostructured silicon anode materials [27]. As can be seen in Fig. 3, for all anode materials, significant lithiation due to the formation of Li_xSi_y occurs at the potentials of below 0.30 V, while de-lithiation (the de-alloying of the lithium ion from the Li_xSi_y structure) is mostly completed before the voltage reaches the value of 0.70 V [5]. As shown in Figs. 4A and 4B, although the observed lithiation and de-lithiation potentials of PSiF anode were almost equal to that of non-porous silicon anode but the integral area of the cyclic voltammogram loop was higher in the case of PSiF anode. This is mainly ascribed to the porous structure of silicon

and consequently facilitated lithium ions insertion and extraction into the anode matrix. The cyclic voltammograms of Ni@PSiF and Bi@PSiF anode materials were also recorded (Figs. 4C and 4D). The higher conductivity of Metal@PSiF anodes in comparison with PSiF leads to the higher lithiation and de-lithiation peak intensity and integral area of cyclic voltammograms [27]. **“Here Fig. 4”**

For further study, the galvanostatic charge-discharge tests of Ni@PSiF and Bi@PSiF anode materials were conducted in a potential range of 0.01 to 1.50 V vs. Li/Li⁺ at the current density of 0.8 C and compared with that of non-porous silicon and PSiF anodes. Fig. 5 shows the second charge-discharge cycles of the different anode materials. The results indicate that the specific capacity of Bi@PSiF (1905 mAh g⁻¹) and Ni@PSiF (1548 mAh g⁻¹) anodes are higher than for PSiF (1224 mAh g⁻¹) and for non-porous silicon (653 mAh g⁻¹) anodes. The higher capacity of Metal@PSiF, which is in agreement with the obtained results by cyclic voltammetry, can be ascribed to the high specific surface area and the higher conductivity of Metal@PSiF. **“Here Fig. 5”**

The influence of metal content of Metal@PSiF nanostructures on the specific capacity of prepared anodes was also examined. In this way, galvanostatic charge-discharge curves of the different Ni@PSiF (samples 1-4) and Bi@PSiF (samples 5-8) anodes were recorded in the potential ranges of 0.01 and 1.50 V vs. Li/Li⁺ at the current density of 0.8 C. As can be seen in Table 3, with increasing the metal content, the specific capacity initially increases and then decreases. The former is believed to be due to an enhancement in the electronic contact of the PSiF with the current collector, which reduces the pulverization of the anodes during the lithiation and de-lithiation process. The latter results can be ascribed to the decreasing of the active material (Si) content of the prepared anodes [28]. Based on the obtained results (Table 3) Ni@PSiF with a nickel content of

14.82% and Bi@PSiF with bismuth content of 31.24% were chosen as anode materials for the rest of the study. **“Here Table 3”**

For further study, the charge-discharge profiles of the Metal@PSiF nanostructures at different C rates were recorded in the potential ranges of 0.01 and 1.50 V. Figs. 6A and 6C show the charge-discharge curves of the Ni@PSiF and Bi@PSiF anode materials from 0.2 C to 3.2 C rate while Figs. 6B and 6D illustrate the variation of the specific capacity vs. the C rate. The obtained results revealed that with increasing the C rate the lithiation and de-lithiation capacities of the proposed anodes decrease. This behavior is due to the decreasing in the degree of utilization of the anode material active sites at higher C rates. Also, at higher C rates, due to an inadequate time for the lithium ions to interact with the active sites of silicon, the anode–electrolyte interaction would be limited. Thus, the alloying and de-alloying of the lithium ions will decrease due to the diffusion polarization [29]. **“Here Fig. 6”**

To evaluate the effect of porous structure formation and metal nanoparticle deposition on the cyclic performance of the silicon-based anodes, the consecutive charge-discharge curves of the non-porous silicon, PSiF, Ni@PSiF and Bi@PSiF anodes were recorded in the potential ranges of 0.01 and 1.50 V. [Fig. 7 illustrates the specific capacity of the different anode materials at 0.1 C rate upon the cycle number. As can be seen, the PSiF anode retains a capacity of 1566 mAh g⁻¹ after 50 cycles, while the non-porous silicon anode maintains a capacity of 693 mAh g⁻¹ after only 25 cycles.](#) The higher capacity and the lower fading rates of PSiF anode in comparison with non-porous silicon anode can be attributed to its porous structure and consequently the higher strain and destruction as well as pulverization of active materials due to alloying and de-alloying of the lithium ions.

The cycling stability and coulombic efficiency of the Metal@PSiF anodes were also studied. A remarkable improvement in the specific capacity and cyclic stability, as well as coulombic efficiency, was observed when Ni and Bi nanoparticles were deposited on the surface of PSiF anodes. The obtained cyclic stability and coulombic efficiency can be ascribed to the large surface area of the conductive metal nanoparticles coating, and thus the large contact area between the PSiF and Ni or Bi, allowed uniform Li insertion and extraction within the PSiF [30]. Moreover, Ni@PSiF shows much superior cycling stability (the capacitance retention of 73 % after 100 cycles) over other Bi@PSiF (the capacitance retention of 64 % after 100 cycles). This is ascribed to the higher binding and buffering effects of the Ni nanoparticles layer that accommodate the large volume change during cycling [31]. As shown in Fig. 7A, after 100 cycles, the Ni@PSiF and Bi@PSiF anodes exhibited a capacity of about 1873 and 2069 mAh g⁻¹, respectively which is about five times larger compared with that of graphite anode (372 mAh g⁻¹). Long term stability and charge storage capacity comparison of the different silicon nanostructures for Li-ion batteries application vs. our proposed anode materials are given in Table 4 [32-38]. Also, the structure changes of the electrode materials after charge/discharge cycling have been investigated using XRD and FE-SEM. As can be seen in Fig 7B, after 50 cycles, the XRD pattern of PSiF does not show any characteristic peaks for the silicon planes, which reveals that the active material becomes from crystalline to amorphous. Also, after 100 cycles, the crystalline Si peaks of Ni@PSiF (curve b) and Bi@PSiF (curve c) completely disappeared (as a result of the crystalline to the amorphous transformation of silicon) and only crystalline peaks of metal nanoparticles were seen. Other studies confirm that crystalline silicon becomes amorphous during lithium insertion and extraction [39]. FE-SEM images of Ni@PSiF (Fig 7C) and Bi@PSiF (Fig 7D) after 100 cycles also revealed that nano metal coated PSiF possess good structure stability during charge/discharge process.

249 **“Here Fig. 7 and Table 4”**

250 **4. Conclusion**

251 In this paper, a facile electroless approach was introduced for the synthesis of the
252 Ni@PSiF and Bi@PSiF nanostructures. The prepared nanostructures were characterized
253 with different techniques and used as anode materials for lithium ion batteries. The
254 electrochemical evaluations indicate that Ni and Bi nanoparticles improve the specific
255 capacity and cyclic stability as well as columbic efficiency of the PSiF anodes. The key for
256 these superior performances is believed to lie in the high surface area of PSiF and the
257 uniform conductive metal nanoparticles coating of the PSiF surface. Ease of preparation,
258 combined with high electrochemical performance and silicon abundance, implies that the
259 proposed nanostructures have potential applications as an anode electrode material for
260 lithium ion batteries.

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Table 1. The initial concentration of nickel precursor for preparation of different Ni@PSiF nanostructures and their corresponding chemical composition (determined by EDS technique)

Sample	NiSO ₄ .6H ₂ O g/L	Element	Line	Wt. %	
1	4.5	Si	K α	94.66	
		Ni	K α	5.34	
				100	Total
2	9.0	Si	K α	90.09	
		Ni	K α	9.91	
				100	Total
3	13.5	Si	K α	85.18	
		Ni	K α	14.82	
				100	Total
4	18.0	Si	K α	81.77	
		Ni	K α	18.23	
				100	Total

Table 2. The initial concentration of bismuth precursor for preparation of different Bi@PSiF nanostructures and their corresponding chemical composition (determined by EDS technique).

Sample	Bi(NO ₃) ₂ .5H ₂ O g/L	Element	Line	Wt. %	
1	4.0	Si	K α	76.93	
		Bi	L α	23.07	
				100	Total
2	5.0	Si	K α	72.59	
		Bi	L α	27.41	
				100	Total
3	6.0	Si	K α	68.76	
		Bi	L α	31.24	
				100	Total
4	7.0	Si	K α	65.14	
		Bi	L α	34.86	
				100	Total

Table 3. The Ni or Bi content of the different anode materials and their corresponding specific capacity at the current density of 0.8 C.

Anode material	Ni content Wt.%	Capacity (mAh g ⁻¹)	Anode material	Bi content Wt.%	Capacity (mAh g ⁻¹)
1	5.34	1275	5	23.07	1338
2	9.91	1380	6	27.41	1547
3	14.82	1548	7	31.24	1905
4	18.23	1506	8	34.86	1803

Table 4. Comparison of the capacity observed and columbic efficiency in the present work with that of reported silicon-based anode materials for Li-ion batteries ($1C = 4000 \text{ mAh g}^{-1}$).

Anode materials	Columbic efficiency (%)	Capacity After Cycles (mAh g^{-1})	Current density (C)	Cycle number	Reference
Ag deposited 3D porous Si	99	755	0.025	50	[32]
Amorphous carbon coated prickly like Si	96	1125	0.1 C	100	[33]
Porous nano-Si@C@RGO	99	1500	1 C	50	[34]
Mesoporous Si@C	98	1200	0.05 C	50	[35]
Hollow porous Si/C	97	700	1C	50	[36]
Micro-sized nano-porous Si/C	96	600	0.125 C	300	[37]
Porous silicon/pyrolyzed polyacrylonitrile	97	2043	0.075	100	[38]
Ni@PSiF	97	1873	0.1 C	100	This work
Bi@PSiF	98	2069	0.1 C	100	This work

Legend for the figures:

Figure 1. EDS spectrum of Ni@PSiF (A), and Bi@PSiF (B) nanostructures and their corresponding elemental mapping; FE-SEM images of Ni@PSiF (C), and Bi@PSiF (D) nanostructures.

Figure 2. XRD patterns of PSiF (curve a), Ni@PSiF (curve b), and Bi@PSiF nanostructures (curve c) in the 2θ ranges of $20-100^\circ$ (A); TEM images of Ni@PSiF (B), and Bi@PSiF (C) nanostructures.

Figure 3. A): Survey XPS data for Ni@PSiF and Bi@PSiF; B): High resolution XPS of Si (2p); C: Ni (3p) and Bi (4f).

Figure 4. Cyclic voltammograms Si (A), PSiF (B), Ni@PSiF (C) and Bi@PSiF at a scan rate of 0.1 mV s^{-1} .

Figure 5. Charge–discharge curves of Si (A), PSiF (B), Ni@PSiF (C) and Bi@PSiF at a rate of 0.8 C.

Figure 6. Charge–discharge curves of Ni@PSiF (A) and Bi@PSiF (C) at various C rates from 0.2 to 3.2 and variation of the specific capacity of Ni@PSiF (B) and Bi@PSiF (D) vs. the C rates.

Figure 7. Capacity retention and coulombic efficiency of different anode materials vs. the cycle numbers at a rate of 0.1 C (A); XRD patterns of PSiF after 50 cycles (curve a), Ni@PSiF after 100 cycles (curve b) and Bi@PSiF after 100 cycles (curve c) in the 2θ ranges of $20-60^\circ$ (B); FE-SEM images of Ni@PSiF (C), and Bi@PSiF (D) nanostructures after 100 cycles.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7