## **Supporting Information**

## Coupling of conductive Ni<sub>3</sub>(2,3,6,7,10,11hexaiminotriphenylene)<sub>2</sub> metal-organic frameworks with silicon nanoparticles for use in high-capacity lithium-ion batteries

Aqsa Nazir,<sup>a</sup> Hang T. T. Le,<sup>b</sup> Chan-Woo Min,<sup>a</sup> Arvind Kasbe,<sup>a</sup> Jaekook Kim,<sup>a</sup> Chang-Soo Jin,<sup>c</sup> Chan-Jin Park<sup>a,\*</sup>

<sup>a</sup> Department of Materials Science and Engineering, Chonnam National University, 77, Yongbongro, Bukgu, Gwangju 61186, South Korea

<sup>b</sup> Department of Electrochemistry and Corrosion Protection, School of Chemical Engineering, Hanoi University of Science and Technology, 1 Dai Co Viet Road, Hanoi, Vietnam

<sup>c</sup> Energy Storage Laboratory, Korea Institute of Energy Research, 102 Gajeong Ro, Yuseong 305343, Daejeon, South Korea

\* Corresponding author.

Tel.: +82-62-530-1704;

Fax: +82-62-530-1699

E-mail address: parkcj@jnu.ac.kr(C.J. Park)



**Fig. S1.** (a) Wide-scan X-ray photoelectron spectroscopy (XPS) spectrum and core-level XPS spectra of (b) Si 2p, (c) O 1s, and (d) C 1s for SiNPs.



**Fig. S2** Energy dispersive X-ray spectroscopy (EDS) elemental mapping of the Si/Ni<sub>3</sub>(HITP)<sub>2</sub> electrode made up of 70% Si, 10% Ni<sub>3</sub>(HITP)<sub>2</sub>, 10% super P<sup>®</sup> carbon black, and 10% lithium polyacrylate (LiPAA). (HITP = 2,3,6,7,10,11-hexaiminotriphenylene.)



**Fig. S3** Cyclic voltammograms for (a) pure  $Ni_3(HITP)_2$  and (b) super P<sup>®</sup> carbon black electrodes in a potential range of 0.005–1.5 V vs. Li/Li<sup>+</sup> at the scan rate of 0.1 mV s<sup>-1</sup>. (HITP = 2,3,6,7,10,11-hexaiminotriphenylene.)



**Fig. S4** (a) Impedance spectra of SiNPs,  $Ni_3(HITP)_2$  and  $Si/Ni_3(HITP)_2$  electrodes; (b) impedance spectra of the Si/Ni\_3(HITP)\_2 electrodes after several cycles of discharge-charge. (HITP = 2,3,6,7,10,11-hexaiminotriphenylene.)

To interpret the electrochemical performance of the Si/Ni<sub>3</sub>(HITP)<sub>2</sub> composite, electrochemical impedance measurements were performed on the SiNPs, Ni<sub>3</sub>(HITP)<sub>2</sub>, and Si/Ni<sub>3</sub>(HITP)<sub>2</sub> electrodes. As shown in **Fig. S4**a, the electrochemical impedance spectra of single SiNPs, single Ni<sub>3</sub>(HITP)<sub>2</sub>, and Si/Ni<sub>3</sub>(HITP)<sub>2</sub> electrodes before cycling are characterized by a semicircle in the high-frequency region and an inclined line in the low-frequency region. The semicircle is associated with charge transfer resistance ( $R_{cl}$ ) at the electrode/electrolyte interface, while the inclined line represents the Warburg element, which reflects the diffusion of Li ions inside the active material particles. It is noticeable that the Si/Ni<sub>3</sub>(HITP)<sub>2</sub> electrode has a smaller  $R_{cl}$  (52.4  $\Omega$ ) than the SiNPs electrode (59.9  $\Omega$ ). The smaller  $R_{cl}$  is undoubtedly related to the presence of

conductive Ni<sub>3</sub>(HITP)<sub>2</sub> in the Si/Ni<sub>3</sub>(HITP)<sub>2</sub> because porous structure provides channels for the Li<sup>+</sup> ions percolation towards the Si and ionic diffusion would be faster as compared to SiNPs electrode. The C, N, and Ni in the porous framework appear to play an important role in facilitating the charge transfer process. It is noteworthy that among three electrodes, the single  $Ni_3$ (HITP)<sub>2</sub> electrode revealed the largest  $R_{ct}$  (107.2  $\Omega$ ). This value is much larger than those of the other electrodes. This demonstrates that the charge transfer process on the Ni<sub>3</sub>(HITP)<sub>2</sub> electrode occurred more difficultly. Meanwhile, it is obvious that the Si/Ni<sub>3</sub>(HITP)<sub>2</sub> composite electrode had a small  $R_{ct}$  compared with both single SiNPs and Ni<sub>3</sub>(HITP)<sub>2</sub> electrodes. This verifies the presence of synergetic effect as the SiNPs and Ni<sub>3</sub>(HITP)<sub>2</sub> materials were mixed. Hence, apart enhanced electronic conductivity,<sup>1</sup> which is caused by much higher electronic conductivity of Ni<sub>3</sub>(HITP)<sub>2</sub> MOF compared with SiNPs, the charge transfer process of the composite electrode was improved significantly. Owing to the presence of conductive porous Ni<sub>3</sub>(HITP)<sub>2</sub> MOF with available open channels around SiNPs, lithium ions diffused straightforwardly. In addition, active sites were exposed for lithiation. As a result, the lithium storage performance of the Si/Ni<sub>3</sub>(HITP)<sub>2</sub> composite electrode was improved remarkably.

To prove the formation of the SEI layer and its growth in subsequent cycles, the electrochemical impedance spectra of the Si/Ni<sub>3</sub>(HITP)<sub>2</sub> electrode after 1, 3, and 7 discharge-charge cycles were recorded. Compared with the impedance spectrum of the as-prepared Si/Ni<sub>3</sub>(HITP)<sub>2</sub> electrode, two semicircles in the high-frequency region corresponding to the resistances caused by the SEI layer and charge transfer process were observed (**Fig. S4b**).<sup>2</sup> The first semicircle represents the resistance due to the formed SEI layer in the succeeding cycles. After the 100<sup>th</sup> cycle, the decreased SEI resistance results from the pulverization of Si/Ni<sub>3</sub>(HITP)<sub>2</sub> particles to a small extent, which increases the electrode surface area, which is inversely

proportional to the solid electrolyte interface resistance  $(R_{SEI})$ .<sup>3</sup> However, the magnitude of the first semicircles remained almost unchanged for the first seven cycles of discharge-charge, suggesting a stable SEI layer.



**Fig. S5** Electrochemical performance of SiNPs and the Si/Ni<sub>3</sub>(HITP<sub>2</sub>) composites containing different Ni<sub>3</sub>(HITP<sub>2</sub>) MOF contents for 100 cycles at the 0.1C-rate: (a) Galvanostatic discharge– charge potential curves and (b) cyclabilities (c) and corresponding coulombic efficiencies. (HITP = 2,3,6,7,10,11-hexaiminotriphenylene.)

As shown in **Fig. S5**a, the first discharge and charge capacities for SiNPs were 3045 and 2287 mAh g<sup>-1</sup>, respectively. Meanwhile, the first discharge/charge capacities for Si/Ni<sub>3</sub>(HITP)<sub>2</sub>-

5%, Si/Ni<sub>3</sub>(HITP)<sub>2</sub>-10%, and Si/Ni<sub>3</sub>(HITP)<sub>2</sub>-15% were measured to be 3754/2330 mAh g<sup>-1</sup>, 3771/2252 mAh g<sup>-1</sup>, and 2775/1590 mAh g<sup>-1</sup>, respectively. After 100 cycles of discharge and charge, the SiNPs, Si/Ni<sub>3</sub>(HITP)<sub>2</sub>-5%, Si/Ni<sub>3</sub>(HITP)<sub>2</sub>-10%, and Si/Ni<sub>3</sub>(HITP)<sub>2</sub>-15% electrodes retained the reversible capacity retention of 1795 mAh g<sup>-1</sup>,1965 mAh g<sup>-1</sup>, 2657 mAh g<sup>-1</sup>, and 1944 mAh g<sup>-1</sup>, respectively. The achieved maximum reversible capacity of 2657 mAh g<sup>-1</sup> was found for the Si/Ni<sub>3</sub>(HITP)<sub>2</sub>-10% electrode after 100 cycles, indicating the outstanding electrochemical performance of the Si/Ni<sub>3</sub>(HITP)<sub>2</sub>-10% composite.



**Fig. S6** Electrochemical performance of the Ni<sub>3</sub>(HITP)<sub>2</sub> electrode: (a) Discharge–charge potential curves; (b) Cyclability and (c) corresponding Coulombic efficiency.

To evaluate the contribution of Ni<sub>3</sub>(HITP)<sub>2</sub> MOF to the capacity of the Si/Ni<sub>3</sub>(HITP)<sub>2</sub> composite electrode, the single Ni<sub>3</sub>(HITP)<sub>2</sub> electrode was prepared with the same process with that of the composite electrode, wherein, a slurry was made by 80 wt% (Ni<sub>3</sub>(2,3,6,7,10,11-hexaiminotriphenylene)<sub>2</sub>), 10 wt% super P\* carbon black, and 10 wt% lithium polyacrylate (LiPAA) in water. **Fig. S6** shows the discharge and charge performance of the Ni<sub>3</sub>(HITP)<sub>2</sub> MOF electrode at a current density of 100 mAg<sup>-1</sup> for 100 cycles. Obviously, at the first cycle the Ni<sub>3</sub>(HITP)<sub>2</sub> MOF electrode delivered a specific discharge capacity of 1694 mAh g<sup>-1</sup> and a specific charge capacity of 1119 mAh g<sup>-1</sup> with Coulombic efficiency of 66%. However, the specific

capacity of the electrode decreased dramatically in the following 30 cycles. Then, the specific discharge/charge capacities remained stably around 210 mAh g<sup>-1</sup>, corresponding the Coulobic efficiency of ~ 96%. This demonstrates poor lithium storage capability of single Ni<sub>3</sub>(HITP)<sub>2</sub> MOF material in this work. If based on the content of Ni<sub>3</sub>(HITP)<sub>2</sub> MOF present in the Si/Ni<sub>3</sub>(HITP)<sub>2</sub> composite (10 wt%), the contribution of Ni<sub>3</sub>(HITP)<sub>2</sub> MOF to the total specific capacity of the composite was relatively small. Surprisingly, in the presence of Ni<sub>3</sub>(HITP)<sub>2</sub> MOF, the specific capacity of the composite was enhanced significantly, suggesting the synergic effect when coupling Ni<sub>3</sub>(HITP)<sub>2</sub> MOF with Si nanoparticles.



**Fig. S7** Scanning electron microscopy (SEM) images of (a) the as-prepared Si electrode and (b-d) the Si electrode in a fully charged (de-alloyed) state after 100 cycles. SEM surficial images of (e) the as-prepared Si/Ni<sub>3</sub>(HITP)<sub>2</sub> electrode and (f-h) the Si/Ni<sub>3</sub>(HITP)<sub>2</sub> electrode in a fully charged (de-alloyed) state after 100 cycles. (HITP = 2,3,6,7,10,11-hexaiminotriphenylene.)

Fig. S7 shows the morphological changes in the SiNPs and Si/Ni<sub>3</sub>(HITP)<sub>2</sub> electrodes before and after 100 cycles of discharge-charge. Before the cycling test, the surface of the SiNPs and

Si/Ni<sub>3</sub>(HITP)<sub>2</sub> electrodes appear to be smooth and uniform (**Fig. S7** a, e). After the cycling test, the surface of the SiNPs electrode changes significantly. Most of the electrode is peeled off from the Cu current collector as shown in (**Fig. S7** b, c). This occurrence is attributed to volume expansion and pulverization of the SiNPs, leading to decay of the SEI layer that is repeatedly reformed and degradation of the smoothness and compactness of the Si electrode surface. Some prominent cracks are observed on the surface of the electrode (**Fig. S7** d). However, the superior microstructural integrity of the Si/Ni<sub>3</sub>(HITP)<sub>2</sub> electrode is seen, as shown in **Fig. S7** f-h. The Si/Ni<sub>3</sub>(HITP)<sub>2</sub> composite well adhered to the Cu current collector without any surface cracks even after 100 cycles of discharge-charge. This observation demonstrates the role of the Ni<sub>3</sub>(HITP)<sub>2</sub> electrode.



**Fig. S8** Cyclability of LiCoO<sub>2</sub> cathode made up of 80% active material, 10% super P<sup>®</sup> carbon black, and 10% polyvinylidene difluoride-N-Methyl-2-Pyrrolidone (PVDF-NMP).

## Reference

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