Multi-walled carbon nanotube-wrapped SiP2 as a superior anode material for lithium-ion and sodium-ion batteries

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HIGHLIGHTS

- MWCNT-wrapped SiP2 anodes for LIBs and SIBs is fabricated.
- MWCNT-wrapped SiP2 shows a capacity of 1622 mA h g⁻¹ at 0.5 A g⁻¹ in LIBs.
- MWCNT-wrapped SiP2 shows a capacity of 925 mA h g⁻¹ at 0.2 A g⁻¹ in SIBs.
- Coin-type and pouch-type full cells were assembled using SiP2 anodes.

GRAPHICAL ABSTRACT

ABSTRACT

SiP2 has a high specific theoretical capacity of 2902 mA h g⁻¹ as an anode material for lithium-ion batteries and 1788 mA h g⁻¹ for sodium-ion batteries, respectively, but demonstrates very poor cycling stability in the entire voltage range (0-2 V). Here, we report high performance SiP2 anodes for lithium-ion batteries and sodium-ion batteries with good cycling stability by wrapping SiP2 with multi-walled carbon nanotube (MWCNT) on the surface of SiP2 via a ball milling process. MWCNT provides a robust network to connect fragment SiP2 with surrounding electrical conductor and serves as an effective conductive agent. MWCNT-wrapped SiP2 shows a reversible capacity of 1622 mA h g⁻¹ after 100 cycles at 0.5 A g⁻¹ in lithium-ion batteries and 925 mA h g⁻¹ after 200 cycles at 0.2 A g⁻¹ in sodium-ion batteries. In addition, rate capability is significantly enhanced. Furthermore, both coin-type and pouch-type full cells are assembled using SiP2 anodes which are coupled respectively with a cathode of LiFePO4 for lithium-ion batteries and a cathode of Na2/3Ni1/3Mn2/3O2 for sodium-ion batteries, and supplied as a reliable energy source for electronic uses to evaluate practical applications.

1. Introduction

Lithium ion batteries (LIBs) and sodium ion batteries (SIBs) with higher energy and power densities are needed for batteries applicable for advanced technologies [1,2], including hybrid electric vehicles (HEV), electric vehicles (EV), intelligent grid and renewable energy technologies. In the past 25 years, intercalation-type anode plays a critical role in commercial batteries, however, graphite’s low theoretical specific capacities of graphite in LIBs (372 mA h g⁻¹) and SIBs (35 mA h g⁻¹) can’t comply with increasing demand of energy storage, therefore, high specific capacity elements are proposed as graphite alternatives, such as silicon (Si), phosphorus (P), and germanium, etc. [3–9].

Silicon (Si) is a promising graphite alternative for LIBs due to its high theoretical capacity of 3578 mA h g⁻¹. Nonetheless, Si occurred massive volume change of about 300% during repeated lithiation-
delithiation processes which results in electrode pulverization. One effective strategy to address this problem is to use active/inactive composite materials, i.e., Si-X (X = Li active/inactive element) compounds, as an active material. For example, Si-X compounds, such as Co [10], Ni [11], Fe [12], Cu [13], can improve electrical conductivity and capacity retention since inactive metal can mitigate large volume expansion. On the contrary, Si-X compound employing Li-active metals, such as O [14], Ca [15], Mg [16], Sn [17], enhance electrochemical performance of anodes owing to enhanced electrical conductivity and matrix of inactive component. On the other hand, phosphorus (P) has the second highest theoretical capacity of 2596 mA h g\(^{-1}\) in LIBs, making it another attractive graphite alternative. Besides, P has the highest theoretical capacity (2596 mA h g\(^{-1}\)) in SiBs, whereas Si has low level activity with sodium ions. However, P also meets capacity degradation resulted from large volume expansion during lithiation-delithiation or sodiation-desodilation processes and behaves like an insulator [18,19]. Several metal phosphides (MP, M = transition metal), such as FeP [20], FeP\(_2\) [21] CoP [22], Cu\(_2\)P [23], and CuP\(_2\) [24], have been suggested, but it prefers to prepare P-based compounds with other high specific capacity elements [25–27].

SiP\(_2\) has a theoretical capacity of 2902 mA h g\(^{-1}\) in LIBs, which is superior to that of P. SiP\(_2\) can react with sodium ions to form Na\(_3\)P that possess a theoretical capacity of 1788 mA h g\(^{-1}\) in SiBs [25,26]. Moreover, SiP\(_2\) has a unique 3D crystalline framework structure to effectively improve electrochemical performance of Si and P within different voltage range in LIBs. In the electrochemical analysis with voltage range between 0.25 V and 2 V, and voltage between 0.55 V and 2 V, SiP\(_2\) shows an outstanding retention of 98.8% and 99.9% after 100 cycles respectively; however, the narrow voltage range substantially limits capacities of SiP\(_2\), which only has a capacity of 1100 mA h g\(^{-1}\) operated from 0.25 V to 2 V and 500 mA h g\(^{-1}\) from 0.55 V to 2 V, respectively. In the entire voltage range (0–2 V), SiP\(_2\) shows unstable cycling performance after 100 cycles with retention less than 50%.

We show that SiP\(_2\) wrapped with multi-walled carbon nanotubes (MWCNT) has significantly improved cycle ability and rate capability for both LIBs and SiIBs in the entire voltage range (0–2 V). MWCNT–wrapped SiP\(_2\) was prepared via a ball milling process. The electric measurement of MWCNT-wrapped SiP\(_2\) pellets exhibits conductivity five times higher than that of pristine SiP\(_2\). MWCNT not only improves conductivity, but also provides a robust network to SiP\(_2\) anodes, resulting in superior cycling performance of 1622 mA h g\(^{-1}\) after 100 cycles at a current density of 0.5 A g\(^{-1}\) and 1522 mA h g\(^{-1}\) at 4 A g\(^{-1}\) in SiBs, and 925 mA h g\(^{-1}\) after 200 cycles at 0.2 A g\(^{-1}\) and 491 mA h g\(^{-1}\) at 2 A g\(^{-1}\) in SiBs. The anode performance of MWCNT-wrapped SiP\(_2\) anodes ranks as the best anode performances on a basis of SiP\(_2\)-related anode to date. Finally, the full cells assembled with MWCNT-wrapped SiP\(_2\) anodes were coupled respectively with a cathode of LiFePO\(_4\) in LIBs and a cathode of Na\(_{2/3}\)Ni\(_{1/3}\)Mn\(_{2/3}\)O\(_2\) in SIBs that were used to verify the feasibility of MWCNT-wrapped SiP\(_2\) as anodes on practical battery designs.

2. Result and discussion

Alloy-type electrodes/carbon composite were often prepared to address the issue of poor electrochemical performance. Active materials milled with a variety of carbon sources such as graphene [28,29], carbon black [30,31], graphite [32,33], and carbon nanotubes [34,35] can improve electrical conductivity and alleviate volume expansion.
since active materials are embedded into carbon matrix effectively. We choose carbon nanotube as composite carbon source since it provides beneficial electrical conductivity, strong architectures, and mechanical resilience for active materials. Fig. S1 shows the illustration of the preparation of MWCNT-wrapped SiP$_2$, SiP$_2$ was firstly prepared by ball milling of silicon and phosphorus, and the resulting SiP$_2$ was then ball milled again with the presence of MWCNT. Compared with black phosphorus, which react with oxygen to form P$_2$O$_5$ [36,37], SiP$_2$ is chemically stable in the atmosphere. In the crystalline structure of SiP$_2$, lone pair occupied by silicon may prevent the reaction between phosphorus and oxygen. Fig. S2 shows the XRD pattern of the MWCNT-wrapped SiP$_2$ phase, which precisely corresponded to cubic SiP$_2$ chemically stable in the atmosphere. In the crystalline structure of SiP$_2$, metal foil as counter electrode within the range of 0.01 V anode was tested by coin-typed half-cell (CR2032) using a lithium shows the voltage pro

Electric characteristics of MWCNT-wrapped SiP$_2$, SiP$_2$, Ge, and Si from 10 kHz to 10 mHz. In the Nyquist plots (Fig. 3d), the semicircle part represents the charge transfer resistance, resulting from the occurrence of polarization of electrode as leaving open-circuit equilibrium state. It was obvious that the corresponding semicircle of the electrode that experienced 50 cycles was extremely smaller than that of the as-prepared electrode, indicating a decrease in charge transfer resistance from 150 to 20 Ω, suggesting improved electron transfer and lithium ion diffusion.

The peaks indicate insertion reaction of Li ions, and the presence of sharp peaks suggest that different react phases. Fig. 3c shows the cycling performance of MWCNT-wrapped SiP$_2$, pristine SiP$_2$, and MWCNT at a current density at 0.5 A g$^{-1}$. The first discharge and charge specific capacity of MWCNT-wrapped SiP$_2$ were 2642 and 2131 mA h g$^{-1}$ respectively, corresponding to a Coulombic efficiency nearly 80%. The capacity contributed by MWCNT in MWCNT-wrapped SiP$_2$ composite is negligible by their significantly lower capacities (~170 mA h g$^{-1}$) as a LIB anode. The irreversible capacity was mainly caused by forming a SEI layer on the electrode during the first discharge and charge processes. After the first cycle, subsequent cycles showed the highly reversible capacity without apparent fading compared with SiP$_2$ after 100 cycles. The 100th cycle exhibited a specific capacity of charge 1622 mA h g$^{-1}$, which maintained the nearly 93% charge capacity of the 5th cycle. The plateau is same between 1st cycle and 100th cycle. In addition to reaction with lithium, there are no other side reaction shows the electrochemical stability is stable. On the other hand, the first discharge and charge specific capacity of SiP$_2$ were 2281 and 1980 mA h g$^{-1}$ respectively; however, in the sequential cycles, SiP$_2$ shows apparent decay. After 100 cycles, MWCNT-wrapped SiP$_2$ and SiP$_2$ exhibit 93% and 22.3% retention. Electrochemical performances of SiP$_2$ studies reported in LIBs were summarized in Table 1. The anode performance of MWCNT-wrapped SiP$_2$ anodes ranks as the best anode performance to date. The interfacial electrochemical behavior difference of MWCNT-wrapped SiP$_2$ electrode after cycling was investigated by means of electrochemical impedance spectroscopy (EIS), which was carried out from 10 kHz to 10 mHz. The Nyquist plots (Fig. 3d), the semicircle part represents the charge transfer resistance, resulting from the occurrence of polarization of electrode as leaving open-circuit equilibrium state. It was obvious that the corresponding semicircle of the electrode that experienced 50 cycles was extremely smaller than that of the as-prepared electrode, indicating a decrease in charge transfer resistance from 150 to 20 Ω, suggesting improved electron transfer and lithium ion diffusion.

The comparison between rate-capability of MWCNT-wrapped SiP$_2$ and SiP$_2$ were evaluated by increasing the discharge/charge rate from 0.2 A g$^{-1}$ to 30 A g$^{-1}$, as shown in Fig. 4a, and its corresponding voltage profiles are shown in Fig. 4b. MWCNT-wrapped SiP$_2$ showed an outstanding rate performance between 0.2 A g$^{-1}$ and 30 A g$^{-1}$, displaying specific charge capacities of 2053, 1753, 1636, 1473, 1250, 1071, 791, and 391 mA h g$^{-1}$ at current densities of 0.2 A g$^{-1}$, 1 A g$^{-1}$, 2 A g$^{-1}$, 4 A g$^{-1}$, 6 A g$^{-1}$, 10 A g$^{-1}$, 14 A g$^{-1}$, 20 A g$^{-1}$ and 30 A g$^{-1}$, respectively. Compared with of SiP$_2$ without MWCNT, MWCNT-wrapped SiP$_2$ showed significant improvement in rate-capability. As shown in Fig. 4c, MWCNT-wrapped SiP$_2$ showed good cycling life of 200 cycles at high current density of 4 A g$^{-1}$.

The photograph of pristine SiP$_2$ electrode shows severe
delamination of active materials from copper foil surface after 100 cycle charge/discharge at a current density of 4 A g\(^{-1}\) (Fig. S4a). Before lithiation, SiP\(_2\) particles show uniformly dispersion with binder and conductive agent (Fig. S4b), but obviously disintegrated and collapsed after cycling (Fig. S4c). On the other hand, the surface of MWCNT-wrapped SiP\(_2\) electrode still remained intact after cycles (Fig. S4e). MWCNT can secure the SiP\(_2\) particle to prevent particle cracking and fracture (Fig. S4d). SEM images with higher magnification further prove that MWCNT can capture fragment of SiP\(_2\) during cycling (Fig. S4h).

The full cells consisting of MWCNT-wrapped SiP\(_2\) anode and commercial LiFePO\(_4\) cathode verify the practical application of MWCNT-wrapped SiP\(_2\) anode. In Fig. S5a, the charge simulation of full cells shows an appropriate voltage range of MWCNT-wrapped SiP\(_2\) full cells obtained by subtracting the charge curve of LiFePO\(_4\) from the discharge curve of the MWCNT-wrapped SiP\(_2\) in their respective half-cells. The MWCNT-wrapped SiP\(_2\)-LiFePO\(_4\) charge curve full cell should be located between 2 V and 3.5 V, and the plateau of discharge curve was about 2.8 V and 3.2 V. In Fig. S5b, the MWCNT-wrapped SiP\(_2\)-LiFePO\(_4\) full cell discharge curve was plotted in the same way, ranging from 3.2 V to 2 V. The plateau of discharge curve was about 2.8 V and 2.4 V. Therefore, the full cell cutoff voltage of discharge and charge should be set between 2 V and 4 V respectively. Few capacities could be obtained below 2 V and above 4 V. Moreover, the lower voltage led to limited application and higher voltage probably resulted in side reaction respectively.

As shown in Fig. 5a, cycling performance of the coin-typed full cells at current density about 0.4 A g\(^{-1}\) and a areal capacity about 1.6 mA h/cm\(^2\), displayed a specific charging density of 2151 mA h g\(^{-1}\) and good retention about 95.5% after 50 cycles (respect to 2nd cycle), indicating high potential for use in practical application. The voltage profiles at 1st, 10th, 20th, and 40th cycle (Fig. 5b) exhibit several potential plateaus during the discharge and charge cycles. In the charge process potential plateaus at 2.5–3.5 V and in the discharge process voltage curve at 3.0–2.0 V. These results both correspond approximately with the simulation. As shown in Fig. 5c, coin-typed full-cell at high current density (4 A g\(^{-1}\)) exhibits high retention (94% respective to 2nd cycle) after 150 cycles, indicating high utilization of MWCNT-wrapped SiP\(_2\). To further facilitate MWCNT-wrapped SiP\(_2\) applications, high capacity (35 mA h) pouch type full cell (Fig. 5d and e) was fabricated, showing satisfactory performance after 50 cycle with 85% retention and successfully applied to light up more than 100 LEDs with red, yellow, and orange color (Fig. 5f).

We also evaluate the electrochemical performance of the MWCNT-wrapped SiP\(_2\) composites as SIB anodes, which were assembled in coin-

Table 1
Comparison of the electrochemical performance of different SiP\(_2\) electrodes for LIBs.

<table>
<thead>
<tr>
<th>Active material</th>
<th>Capacity (5th cycle)</th>
<th>Capacity (100th cycle)</th>
<th>retention</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNT-wrapped SiP(_2)</td>
<td>1760 mA h g(^{-1})</td>
<td>1622 mA h g(^{-1})</td>
<td>93%</td>
<td>This work</td>
</tr>
<tr>
<td>SiP(_2)</td>
<td>1822 mA h g(^{-1})</td>
<td>435 mA h g(^{-1})</td>
<td>24%</td>
<td>This work</td>
</tr>
<tr>
<td>SiP(_2)/C</td>
<td>1700 mA h g(^{-1})</td>
<td>700 mA h g(^{-1})</td>
<td>41%</td>
<td>[25]</td>
</tr>
<tr>
<td>SiP(_2)/C</td>
<td>2000 mA h g(^{-1})</td>
<td>1000 mA h g(^{-1})</td>
<td>50%</td>
<td>[26]</td>
</tr>
</tbody>
</table>

Fig. 3. Electrochemical performances of MWCNT-wrapped SiP\(_2\) in LIBs (a) voltage profiles of MWCNT-wrapped SiP\(_2\) at 0.2 A g\(^{-1}\) between 0.01 V and 2.5 V (b) differential capacity profile of the first, 10th, and 20th cycles of MWCNT-wrapped SiP\(_2\) (c) charge/discharge cycle performance of MWCNT-wrapped SiP\(_2\), SiP\(_2\), and MWCNT at 0.5 A g\(^{-1}\) for 100 cycles (d) electrochemical impedance spectroscopy of fresh MWCNT-wrapped SiP\(_2\) electrode and that of the electrode, which experienced a 50 cycling test.
typed half-cells (CR2032) with sodium metal foil as counter electrode within the range of 0.01 V–2.5 V. Fig. 6a shows the voltage profile of MWCNT-wrapped SiP2. During the discharge process, the voltage rapidly declined to a plateau at 0.5 V which illustrated the transformation of active material due to the insertion of sodium ions. The voltage further decreased slowly to 0.01 V to form the final phase. In the charge process, a plateau was observed at 0.7 V–1.1 V, which represent the evacuation of sodium ions. Fig. 6b exhibits the differential capacity profiles of the 1st, 10th, 50th, and 100th cycle. The different peaks indicate different insertion reactions of Na ions, and each sharp peak suggests different reaction phase. Fig. 6c shows cycling performance of the MWCNT-wrapped SiP2, SiP2 and MWCNT with the current density at 0.2 A g\(^{-1}\). The first discharge and charge specific capacity of MWCNT-wrapped SiP2 were 1009 and 737 mA h g\(^{-1}\) respectively, which indicates a Coulombic efficiency of 73%. The capacity contributed by MWCNT in MWCNT-wrapped SiP2 composite is negligible by their significantly lower capacities (\(\sim 50\) mA h g\(^{-1}\)) as an SIB anode. The irreversible capacity loss in the first cycle probably resulted from the consumption of sodium of solid electrolyte interface (SEI) layer. Surprisingly, the specific capacity displayed slightly rise in each subsequent cycle. This phenomenon could be attributed to strong chemical bonding between Si and P. In LIBs, both Si and P reacted with lithium ions. However, in SIBs, only P reacted with sodium ions, making chemical bonding between Si and P more too strong to be broken than that in LIBs. Tough chemical bonds limit phosphorus reactivity, leading to specific capacity less than the theoretical capacity, i.e., 1788 mA h g\(^{-1}\), with silicon being participated in SIBs. Furthermore, this phenomenon also provides space of unreactive material to alleviate mechanical stress during charge/discharge process. After 200 cycles, the specific capacity of charge was 920 mA h g\(^{-1}\), approaching to a nearly 132% relative to charge capacity of the 5\(^{th}\) cycle, and is higher than the reported value (Table 2). We can see the same plateaus between 1st cycle and 200\(^{th}\) cycle, indicating that there are no other side reactions and show good electrochemical stability. On the other hand, the first discharge and charge specific capacity of SiP2 were 580 and 347 mA h g\(^{-1}\) respectively. The specific capacity of SiP2 without MWCNT shows noticeable deterioration after 100 cycles. Apparently, MWCNT-wrapped SiP2 showed better electrochemical performance than SiP2 without MWCNT; besides, it also had higher specific capacity than that of pristine SiP2. This increment may be resulted from higher chemical reactivity and electrical conductivity provided by MWCNT. Importantly, electrochemical performance of MWCNT-wrapped SiP2 shows significantly improved performance compared to the previous studies of SiP2 sodium ion anodes. The rate-capability improvement of SiP2 wrapped by MWCNT in SIBs was also confirmed by changing the discharge/charge rate from 0.2 A g\(^{-1}\) to 15 A g\(^{-1}\) as shown in Fig. 7a. Compared to SiP2, MWCNT-wrapped SiP2 showed extreme rate performance between 0.2 A g\(^{-1}\) and 15 A g\(^{-1}\), displaying the specific charge capacities of 608, 634, 555, 491, 414, 314, 230, 157, 47 mA h g\(^{-1}\) at the current density of 0.2 A g\(^{-1}\), 0.5 A g\(^{-1}\), 1 A g\(^{-1}\), 2 A g\(^{-1}\), 3 A g\(^{-1}\), 5 A g\(^{-1}\), 7 A g\(^{-1}\), 10 A g\(^{-1}\), and 15 A g\(^{-1}\), respectively. As shown in Fig. 6c, MWCNT-wrapped SiP2 exhibited excellent cycling life of 200 cycles at current density of 2 A g\(^{-1}\). Initially, the current density 0.1 A g\(^{-1}\) for the first cycle was adapted to form an elegant SEI layer on active material surface. At the 300th cycle, the retention of MWCNT-wrapped SiP2 composite specific capacity approached 143% relative to the 2nd cycle and 93.7% relative to the 100\(^{th}\) cycle. These results apparently indicated that cycling performance and rate-capability of active materials were effectively promoted by MWCNT.

Sodium ion full cells were assembled with MWCNT-wrapped SiP2 as...
anodes and Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ (NNMO) as cathodes. The synthesis and related electrical tests of Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ were carried out based on the previous report [40]. In Fig. S6a, the charge simulation of full cells shows appropriate voltage range of MWCNT-wrapped SiP$_2$ full cell obtained by subtracting the charge curve of NNMO from the discharge curve of the MWCNT-wrapped SiP$_2$ in their respective half cells. The MWCNT-wrapped SiP$_2$- NNMO charge curve full cell ranges from 0.8 V to 3.8 V, and the plateau of discharge curve is located between 2.0 to 3.7 V, respectively. In Fig. S6b, the discharge curve of MWCNT-wrapped SiP$_2$//NNMO full cell was plotted in the same way, ranging from 3.2 to 1.0 V. The plateau of discharge curve is located between 1 to 2.2 V and 2.5–3.2 V, respectively. Therefore, the full cell cutoff voltage of discharge and charge should be set between 1.0 V and 4 V, respectively.

In Fig. 8a, a coin-typed full cell displays a specific capacity of 487 mA h g$^{-1}$ at 0.05 A g$^{-1}$ with good retention about 90.3% after 40 cycles (respect to 2nd cycle). The voltage profile of coin-typed full-cell at 1st, 10th, 20th and 30th cycle in Fig. 8b exhibits several potential plateaus during the discharge and charge cycles. In the charge process, potential plateaus locate between 2.0 and 3.7 V and in the discharge process, the voltage curve locates from 1.0 V to 3.7 V, both approximately correspond to the simulation result. As shown in Fig. 8c, the coin-typed full cell at high current density (2 A g$^{-1}$) exhibits high retention, i.e., 80%, with respect to the 2nd cycle after 100 cycles. In order to further facilitate MWCNT-wrapped SiP$_2$ applications, a 6 mA h pouch type full cell (Fig. 8d and e) was prepared and exhibits stable cycling performance up to 50 cycles. This cell can be used to light up more than 100 LEDs with 3 different colors (Fig. 8f).

2.1. Conclusion

In summary, we develop a facile way to wrap SiP$_2$ with MWCNT by using a ball milling process. MWCNT-wrapped SiP$_2$ shows high electrochemical performance with superior reversible capacity 1622 mA h g$^{-1}$ in LIBs after 100 cycles, 925 mA h g$^{-1}$ in SIBs after 200 cycles. In addition, MWCNT-wrapped SiP$_2$ composites also exhibit superior rate capabilities: 1522 mA h g$^{-1}$ in LIBs at a current density of 4 A g$^{-1}$ and 491 mA h g$^{-1}$ in SIBs at a current density of 2 A g$^{-1}$, respectively, owing to five times higher electrical conductivity promoted by MWCNT. MWCNT not only plays a crucial role to provide robust network structure to mitigate mechanical strain and also effectively seizes the fragment of SiP$_2$ to surrounding electrical connections that prevents the capacity degradation. Pouch-type LIB (35 mA h) and SIB (6 mA h) were assembled to demonstrate practical uses. This study suggests that decoration of MWCNT can effectively enhance cycle performance and rate capability of SiP$_2$, making it a promising graphite alternative anodes for both LIBs and SIBs.
3. Experimental section

3.1. Materials

Silicon (Si, powder, 325 mesh, 99% trace metals basis), poly (acrylic acid) (PAA, average MV ∼ 3000000), ethanol (C2H5OH, 99.8%), sodium cubes (99.9%), sodium perchlorate (NaClO4, 98%), manganese (II) carbonate (MnCO3, 99.9%), sodium carbonate (Na2CO3, 99.5%), nickel (II) hydroxide (Ni(OH)2), and ethylene carbonate (EC, 98%) were purchased from Sigma-Aldrich. Phosphorus (P, powder, 325 mesh, 98.9%) was purchased from Alfa Aesar. MWCNT (90% O. D × L 10 nm × 1.5 μm) was purchased from Taiwan Carbon Nanotube Technology Corporation. Commercial LiFePO4 was purchased from Vista Advance technology. Glass fiber filter was purchased from Toyo Roshi Kaisha, Ltd. Lithium hexafluorophosphate (LiPF6), fluoroethylene carbonate (FEC, C2H2FO3), diethyl carbonate (DEC, C3H4O3), lithium metal foil, copper metal foil, Celgard membrane, and coin-type cell CR2032 were purchased from Shining Energy Co., Ltd.

3.2. Synthesis of MWCNT-wrapped SiP2

Red P was transformed into black P by HEBM for 6 h, and then mixed with Si in 2:1 M ratio in a 12-ml grinding jar with 4 balls, where the ball-to-powder weight ratio was 160:1 with both the jar and the balls made in hardened stainless steel, and then SiP2 powder was formed by 6-hrs HEBM under Ar atmosphere. SiP2 powder and MWCNT were mixed in a 12-ml grinding jar with 5:3 wt ratio and 200:1 ball-to-powder weight ratio, followed by HEBM for 1 h with 200 RPM under Ar atmosphere, which led to the formation of MWCNT-wrapped SiP2.

3.3. Characterization

MWCNT-wrapped SiP2 was characterized by field emission scanning electron microscope (FESEM), Spherical Aberration Corrected Scanning Transmission Electron Microscope (Cs-corrected STEM), and X-ray diffraction (XRD). For SEM imaging, images were obtained by using a FESEM (HITACHI-SU8010) at an accelerating voltage of 10–15 kV with 8 mm working distance. The Cs-corrected STEM samples were prepared by dispersing the powder in the ethanol and drop-casting onto a carbon-coated copper grid, and the images were acquired by JEOL ARM200F at an accelerating voltage of 200 kV. XRD patterns were recorded by a Shimadzu XRD-6000 diffractometer equipped with CuK radiation.

3.4. Electrochemical characterization

MWCNT-wrapped SiP2 and PAA were mixed in weight ratio of 80 wt %:20 wt% in ethanol to form homogeneous slurry, which was tape-casted on a copper foil and dried in an oven to prepare LIB or SIB electrodes. The electrodes were dried at 150° C for 1 hr under argon gas
to remove residual water and then pressed by a rolling machine. The coin-type lithium-ion half cells (CR2032) contain MWCNT-wrapped SiP₂ composites electrode with a loading weight of \( \sim 1.5 \text{ mg cm}^{-2} \), lithium metal foil, and a PP/PE/PP membrane wetted by electrolyte, were assembled in an argon-filled glovebox. The electrolyte was composed of 1 M LiPF₆ in a mixture of fluoroethylene carbonate/diethyl carbonate (FEC/DEC) (1:1 v/v). The electrochemical performance of the lithium half-cell was evaluated by using Maccor Series 4000 at the voltage range between 0.01 V and 2.0 V (vs. Li/Li⁺).

As to the coin-type lithium ion full cell (CR2032), LiFePO₄ was used as the cathode with an A/C ratio of \( \sim 1.2 \), where the areal capacities of anode and cathode were 1.45 mAh cm⁻² and 1.2 mA h cm⁻², respectively, and MWCNT-wrapped SiP₂ was used as the anode with loading weight of \( \sim 1.5 \text{ mg cm}^{-2} \). The rest of the components in the full-cell were identical with those in the half-cell. The electrochemical performance of the full cells was investigated by using Maccor Series 4000 at the voltage range between 2.0 V and 4.0 V.

As to the coin-type sodium-ion full cells, NNMO was used as the cathode with an A/C ratio of \( \sim 1.0 \), where the areal capacities of anode and cathode were 0.35 mAh cm⁻² and 0.348 mA h cm⁻², respectively, and MWCNT-wrapped SiP₂ was used as an anode with loading weight about 1.2 mg cm⁻². The synthesis of cathode material NNMO was based on the previous study [40]. The rest of components in full cells were identical with those in the half cells. The electrochemical performance of the sodium-ion full cells was examined at the voltage range between 1.0 V and 3.75 V. For sodium ion pouch type battery assembly, the anode (MWCNT-wrapped SiP₂) and the cathode (NNMO) were both cut into rectangular shape with an area of 30 cm² (3.3 cm × 9 cm), then nickel tab and aluminum tab were connected to the anode and the cathode, respectively. The anode and the cathode separated by PP/PE/PP membrane were stacked evenly in laminated Al film, which was then sealed, and left one side open for later use. The semi-finished product was taken into glovebox for filling electrolyte and sealing the unsealed side. The pouch type battery was tested by using Maccor Series 4000 at the voltage range between 1.0 V and 3.75 V.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.jpowsour.2018.07.003.

References


Fig. 8. Electrochemical characteristics of MWCNT-wrapped SiP2-NNMO full cell. (a) cycling performance and (b) voltage profiles of a coin cell at a current density of 0.2 A g−1 between 1.0 V and 3.75 V. (c) cycling performance of coin cell at a current density of 2 A g−1 between 1.0 V and 3.75 V. (d) voltage profiles of 6 mA h pouch type cell at a current density of 0.2 A g−1 (e) the photograph of a 6 mA h pouch type battery. (f) the demonstration of the pouch-type battery lighting up over 100 LEDs with different colors. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)