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Large-scale highly ordered Sb nanorod array anodes with high capacity and rate capability for sodium-ion batteries

Large-scale highly ordered Sb nanorod array anodes have been rationally designed to achieve improved Na-ion storage performance. A full cell based on the Sb nanorod array anode was also successfully constructed and exhibited highly stable capacity and excellent rate capability, showing the great potential of Sb nanoarrays in large-scale energy storage.

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Large-scale highly ordered Sb nanorod array anodes with high capacity and rate capability for sodium-ion batteries†

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Na-ion batteries are a potential substitute to Li-ion batteries for energy storage devices. However, their poor electrochemical performance, especially capacity and rate capability, is the major bottleneck to future development. Here, we propose a performance-oriented electrode structure, which is a 1D nanostructure array with large-scale high ordering, good vertical alignment, and large interval spacing. Benefiting from these structural merits, a great enhancement in electrochemical performance could be achieved. Taking Sb as an example, we firstly report large-scale highly ordered Sb nanorod arrays with uniform large interval spacing (190 nm). In return for this electrode design, high ion accessibility, fast electron transport, and strong electrode integrity are presented here. Used as additive- and binder-free anodes for Na-ion batteries, Sb nanorod arrays showed a high capacity of 620 mA h g\(^{-1}\) at the 100th cycle with a retention of 84% up to 250 cycles at 0.2 A g\(^{-1}\), and a superior rate capability for delivering reversible capacities of 579.7 and 557.7 mA h g\(^{-1}\) at 10 and 20 A g\(^{-1}\), respectively. A full cell coupled by a P2-Na\(_{2/3}\)Ni\(_{1/3}\)Mn\(_{2/3}\)O\(_2\) cathode and a Sb nanorod array anode was also constructed, which showed good cycle performance up to 250 cycles, high rate capability up to 20 A g\(^{-1}\), and large energy density up to 130 Wh kg\(^{-1}\). These excellent electrochemical performances shall pave the way for developing more applications of Sb nanorod arrays in energy storage devices.

Broader context

Due to the lower cost and larger abundance of Na, Na-ion batteries have been a potential alternative to Li-ion batteries for energy storage devices. The development of electrode materials or structures with good electrochemical performance is currently the key task in Na-ion battery research. In this work, we presented performance-oriented 1D nanostucture arrays with large-scale high ordering, good vertical alignment, and large interval spacing, fabricated by a facile and cost-effective nanoimprinted AAO templating technique, which might be successfully used as an electrode and showed an excellent electrochemical performance. The conceptual design of these arrays is universal to most of the electrode materials. Taking antimony (Sb) as an example, we demonstrated that large-scale highly ordered Sb nanorod arrays with uniform large interval spacing revealed high capacity and superior rate capability for Na-ion storage. Moreover, a full cell constructed using a P2-Na\(_{2/3}\)Ni\(_{1/3}\)Mn\(_{2/3}\)O\(_2\) cathode and a Sb nanorod array anode was also investigated, which exhibited good cycle performance up to 250 cycles, high rate capability up to 20 A g\(^{-1}\), and large energy density up to 130 Wh kg\(^{-1}\). This work may open up more applications of such performance-oriented 1D nanostructure arrays in energy storage systems.

1. Introduction

Sodium-ion batteries (SIBs) have regained increasing research interest as a potential substitute to Li-ion batteries, in particular, for large-scale energy storage systems, due to their low cost, abundant natural resources, and relatively low redox potential.\(^1,2\) Since Na ions are about 55% larger in radius than Li ions, a steric limitation in many host structures is inevitably obtained, leading to slow insertion and extraction of Na ions, large volume changes, and an unstable solid electrolyte interphase (SEI). Therefore, it is a major challenge to find appropriate Na storage electrode materials or structures for high performance SIBs.\(^3,4\)

It is widely accepted that the vertically aligned 1D nanostructure array is an efficient electrode configuration, which enhances the electrochemical performance of batteries.\(^5-8\) However, the majority of reported arrays still contained some...
defects in their electrode structure design, which severely weakened the electrochemical performance. Those arrays showed more or less agglomerated morphology instead of a perfect vertical alignment, in which the joint parts tend to break because of the stress existing among these nanostructures upon cycling, resulting in pulverization and collapse of the electrode. Meanwhile, limited interval spacing in attached arrays lowered the ion transport rate to the deep portions of the electrode, which is not conducive to high rate capability. Although using nanostructure arrays as electrodes omits the complex process of mixing carbon black and binder, the conductivity of most of the arrays is not good enough to support the electrode to finish fast charge and discharge processes and still maintain high capacity and a long cycle life.\textsuperscript{9–12}

Recently, we reported a nanoimprinted AAO templating technique to fabricate 1D nanostructure arrays with perfect long-range regularity, fine size controllability, and very large area (up to cm\textsuperscript{2}).\textsuperscript{13–15} Especially, using this technique, perfectly vertically aligned 1D nanostructure arrays with large interval spacing (e.g. about 200 and 400 nm interval spacing by using different template cell sizes of 400 and 800 nm, and the definition of interval spacing and cell size is shown in Scheme 1X) are achievable. However, so far, there have been very few reports on SIBs using such a 1D nanostructure array electrode.\textsuperscript{16} We believe that, using these 1D nanostructure arrays with large-scale high ordering, good vertical alignment, and large interval spacing as the SIB electrode, the electrochemical performance shall usher in great enhancement.

Antimony (Sb) has been widely investigated because it is cheap, abundant, and environmentally friendly.\textsuperscript{17} The abundance of Sb in the Earth's crust is estimated at 0.2 to 0.5 parts per million. In addition, Sb has been found in over 100 mineral species. Sb is considered a promising anode material for SIBs due to its large Na storage capacity of 660 mA h g\textsuperscript{−1}, good electronic conductivity, and moderate operating voltage.\textsuperscript{17} However, the practical application of Sb is mainly hindered by massive volume changes (about 390%) during repeated sodiation/desodiation processes. Such a volume variation results in severe pulverization and subsequent loss of electrical contact within electrodes, consequently greatly decreasing the cycle life and the rate capability of electrodes.\textsuperscript{4,18} Indeed, pure Sb powders showed a high initial capacity of 624 mA h g\textsuperscript{−1}, while the capacity abruptly decreased to less than 100 mA h g\textsuperscript{−1} after 25 cycles.\textsuperscript{19}

In this work, we firstly report large-scale highly ordered Sb nanorod arrays with uniform large interval spacing as an excellent SIB anode, fabricated by the nanoimprinted AAO templating technique with the assistance of an electrodeposition process. In such a unique architecture, some critical features are worthwhile to be noted. First, each Sb nanorod possesses uniform nanosized diameter, which could shorten the Na ion diffusion pathway. Second, Sb nanorod arrays show a perfect vertical alignment and concomitant large interval spacing, which provide direct channels for the electrolyte to permeate into the deep portions of arrays, then Na ions can fully contact Sb nanorods without dead angles, improving Na ion accessibility. Meanwhile, the large interval spacing in arrays can also prevent the pulverization by facile strain relaxation during cycling. Third, Sb nanorods themselves as electric conductors directly connect with the conductive Au/Ni substrate, offering fast and accessible electron transport, which is very beneficial to the remarkable improvement in the rate capability. Finally, the good adhesion between arrays and the conductive substrate can ensure the robust array integrity to accommodate volume changes upon cycling.

Within the expectation, in return for its pathbreaking electrode design, the as-prepared Sb nanorod arrays, as additive- and binder-free anodes for SIBs, show a high capacity of 620 mA h g\textsuperscript{−1} at the 100th cycle with a retention of 84% up to 250 cycles, and superior rate capability for delivering reversible capacities of 579.7 and 557.7 mA h g\textsuperscript{−1} at 10 and 20 A g\textsuperscript{−1}, respectively. To the best of our knowledge, this is the best electrochemical performance in comparison with previously reported Sb-based anodes for SIBs (Table 1). Moreover, a full cell constructed by a P2-Na\textsubscript{2/3}Ni\textsubscript{1/3}Mn\textsubscript{2/3}O\textsubscript{2} cathode and a Sb nanorod array anode was also investigated, which delivered a good cycle performance up to 250 cycles, high rate capability up to 20 A g\textsuperscript{−1}, and large energy density up to 130 Wh kg\textsuperscript{−1}. We believe that these excellent electrochemical performances shall gain high attention to develop more efficient electrode structures for energy storage systems.

2. Experimental

2.1 Synthesis of nanoimprinted AAO templates

Nanoimprinted AAO templates were prepared using a nanoimprinting technique followed by an anodization process. A clean high-purity (99.99%) aluminum foil was electrochemically polished in a 1:7 (v:v) solution of HClO\textsubscript{4} and ethanol at a voltage range of 20–30 V. The Ni imprinting stamp was placed on a polished Al foil, and the imprinted Al foil was obtained using an oil pressing system under a pressure of about 10 kN cm\textsuperscript{−2} for 3 min. Then the anodization was carried out under a constant voltage of 160 V in 0.4 M H\textsubscript{2}PO\textsubscript{4} at 5 °C for 30 min, in which the anodization voltage was chosen to satisfy the distance periods in the imprinting stamp owing to the linear relationship (2.5 nm V\textsuperscript{−1}) between the interpore distance (400 nm) and the anodization potential (160 V). After anodization, a 50 nm thick layer of Au

![Scheme 1](Image)
was evaporated by physical vapor deposition (PVD), and then a thick layer of Ni was electrochemically deposited on the top of the AAO template with Au as a current-carrying substrate, where Au was used to improve the adhesion between the Ni layer and the template. The backside Al was removed by a mixture solution of CuCl2 (85 wt%) and HCl (15 wt%), and then was transferred to H3PO4 solution (5 wt%) at 30 °C to remove the barrier layer and widen the size of the pores. The time for the barrier layer removal and the pore-widening process depends on the desired pore sizes in the AAO template. At last, a through-pore AAO template with a conductive substrate was achieved.

2.2 Synthesis of Sb nanorod arrays

Sb nanorod arrays were electrodeposited inside the above nanoimprinted AAO templates at a constant current density of 1.0 mA cm⁻² in an electrolytic bath containing SbCl3 and Cu₆H₄Na₃O₇·2H₂O. The electrodeposition was conducted in a two-electrode cell with an AAO template as a working electrode and a Pt foil as a counter electrode. Sb nanorod arrays are released by dissolving the AAO template in a NaOH solution (3.0 M) for 30 min, followed by a rinsing process with deionized water. As reference samples, A-Sb NRs, A-2-Sb NRs, and A-2-Sb NRs were also prepared using the similar procedures.

2.3 Synthesis of layered P2-Na₂/3Ni₁/3Mn₂/3O₂

P2-Na₂/3Ni₁/3Mn₂/3O₂ was prepared by a co-precipitation method with nickel and manganese nitrates in a stoichiometric amount with sodium hydroxide. Na₂CO₃ was added afterwards as the sodium source. Calcination processes were carried out at 600 °C in air. 20–22

2.4 Characterization

SEM and TEM measurements were performed on a Hitachi S4800 instrument with voltages of 5 kV and 30 kV, respectively. HRTEM measurements were performed on a Tecnai 20 S-Twin from Philips. XRD measurements were carried out on a Bruker AXS Discover D8 applying the Cu Kα (1.54056 Å) radiation equipment. For post-cycling SEM measurements, Sb nanorod array electrodes after electrochemical cycling tests were carefully disassembled and washed with PC solution in a glove box, and dried at 60 °C in a vacuum oven. For HRTEM tests, the samples were scraped from the substrate and dispersed in ethanol followed by ultrasonication.

2.5 Electrochemical measurements

Electrochemical measurements of half cells were performed using CR2032 coin-type cells with sodium metal as both counter and reference electrodes. Sb nanorod arrays were used as anodes without any additives of conductive carbon and binder. The mass loading of the active material is around 0.4 mg cm⁻². P2-Na₂/3Ni₁/3Mn₂/3O₂ was employed as a cathode which was prepared by mixing 80% P2-Na₂/3Ni₁/3Mn₂/3O₂, 10% acetylene black, and 10% poly(vinylidene fluoride) (PVDF) by weight with an appropriate amount of 1-methyl-2-pyrrolidinone (NMP). The above mixture was pressed onto an aluminum foil which served as a current collector with a subsequent drying process at 120 °C in vacuum for 12 h. The coin batteries were assembled in a nitrogen-filled glove box with a glass fiber separator (Whatman, GF/B). The electrolyte solution of 1.0 M NaClO₄ in EC: PC (1:1 by volume) with the addition of 5% fluoroethylene carbonate (FEC). Cyclic voltammetry (CV) test was performed on a BioLogic VSP potentiostat. Electrochemical impedance spectroscopy (EIS) was also performed on a BioLogic VSP potentiostat with a frequency of 1 MHz to 10 mHz at the discharge state (0.01 V) after the 1st, 20th, and 50th cycles. The galvanostatic charge-discharge tests were performed at various current densities on a LAND-CT2001A test system (Wuhan, China). All of these experiments were conducted at room temperature.

The full cell was assembled using an electrolyte solution of 1.0 M NaClO₄ in EC: PC (1:1 by volume) with 5% FEC and galvanostatically cycled with the voltage range of 4.0 to 1.4 V at a current density of 0.5 A g⁻¹ (with respect to the anode mass). To ensure a suitable positive-to-negative (P/N) capacity ratio for proper cell balance, the P2-Na₂/3Ni₁/3Mn₂/3O₂ to Sb nanorod array mass loading ratio was kept at about 18.

### Table 1  Electrochemical performance comparison of the as-prepared Sb nanorod arrays with previously reported Sb-based anodes

<table>
<thead>
<tr>
<th>Materials</th>
<th>Current density, A g⁻¹</th>
<th>2nd</th>
<th>50th</th>
<th>100th</th>
<th>Rate capability, mA h g⁻¹ (current density, A g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanocomposite Sb/C¹⁹</td>
<td>0.1</td>
<td>~610</td>
<td>~570</td>
<td>~575</td>
<td>489 (1)</td>
</tr>
<tr>
<td>SnSb/C nanocomposite²⁺</td>
<td>0.1</td>
<td>~540</td>
<td>435</td>
<td>~433</td>
<td>433 (0.2)</td>
</tr>
<tr>
<td>Sb/C fibers²⁺</td>
<td>0.1</td>
<td>~425</td>
<td>~420</td>
<td>400</td>
<td>300 (1)</td>
</tr>
<tr>
<td>Monodisperse Sb nanocrystals³⁺</td>
<td>0.66</td>
<td>~590</td>
<td>~380</td>
<td>~580</td>
<td>550 (5.28)</td>
</tr>
<tr>
<td>Bulk Sb³⁺</td>
<td>0.33</td>
<td>~540</td>
<td>~570</td>
<td>~506</td>
<td>300 (1)</td>
</tr>
<tr>
<td>Sb/MWCNT nanocomposite²⁷</td>
<td>0.2</td>
<td>~510</td>
<td>~450</td>
<td>~400</td>
<td>350 (1)</td>
</tr>
<tr>
<td>SnSb porous hollow microspheres³⁸</td>
<td>0.66</td>
<td>574.9</td>
<td>520.3</td>
<td>502.3</td>
<td>470.3 (1.6)</td>
</tr>
<tr>
<td>Sb nanorod arrays (this work)</td>
<td>0.5</td>
<td>655.7</td>
<td>618.4</td>
<td>612.6</td>
<td>579.7 (10)</td>
</tr>
</tbody>
</table>

### Results and discussion

The sample preparation procedure is schematically illustrated in Scheme 1. A detailed explanation for preparing the nanoimprinted...
AAO template with the conductive layers of Au and Ni (steps I to IV) can be found in the Experimental section. Sb nanorod arrays are achieved by electrodepositing the Sb precursor inside the AAO template (step V) and subsequently dissolving the AAO template (step VI). The electrodeposition process represents a cost-effective and mature technique to obtain nanoarrays. The structural parameters of the Sb nanorods can be easily adjusted by changing the experimental parameters of both template fabrication and electrochemical deposition. At last, Sb nanorod arrays were directly used for assembling sodium cells without use of carbon black and binder, which shall largely avoid undesirable interfaces in the electrode material.

Fig. 1 shows scanning electron microscope (SEM) images of the nanoimprinted AAO template (Fig. 1a and b), and Sb nanorod arrays (Fig. 1c–f). As displayed in Fig. 1a and b, the hexagonally arranged pores of the AAO template are perfectly uniform in a large-area, and the pore size is about 210 nm. It is worth mentioning that both the size and the depth of pores can be accurately adjusted to obtain the desired size depending on the time of pore-widening and anodization, respectively. Fig. 1c–f illustrates the top and tilted views of the as-prepared Sb nanorod arrays which keep the highly ordered and vertically well-aligned growth in large-scale. As is clearly seen from the insets in Fig. 1d and f, Sb nanorods possess a uniform diameter of about 210 nm, and the interval distance between nanorods is as large as 190 nm, as defined by the pore size of the as-prepared AAO template. In this work, the cell size of the nanoimprinted AAO template we used is 400 nm, and larger cell size (800 nm) can also be obtained, as shown in Fig. S1 (ESI†). By using that (800 nm AAO template), a larger interval spacing should be easily controllable.

Fig. 1g displays an optical image of Sb nanorod arrays directly grown on the Au/Ni substrate. It clearly illustrates that Sb nanorod arrays with the Au/Ni substrate can be severely rolled without visible signs of degradation, implying good adhesion and mechanical robustness of the arrays. This feature might indicate the suitability of our electrodes for a possible application in flexible electronics. As shown in the inset of Fig. 1g, highly ordered Sb nanorod arrays are obtained over a large area (around cm²-sized range). Larger areas can also be easily achievable by using the larger-sized Ni imprinting stamp combined with a well-established roll to roll process. The X-ray diffraction (XRD) pattern of the as-prepared Sb nanorod arrays is shown in Fig. S2 (ESI†). Except for the reflections of the substrate (Au and Ni), all the other diffraction peaks can be readily indexed to the rhombohedral Sb phase (JCPDS No. 35-0732) without any impurity, indicating the successful synthesis of Sb. The transmission electron microscope (TEM) image (Fig. 1h) clearly shows the diameter and length of Sb nanorods to be about 210 nm and 1.5 μm, respectively. The high resolution TEM (HRTEM) image in Fig. 1i exhibits the lattice fringes with a distance of 3.09 Å, corresponding to the (012) planes of rhombohedral Sb, further confirming the high crystallinity of the sample. The selected area electron diffraction (SEAD) pattern in the inset of Fig. 1i proves that the Sb nanorods are polycrystalline. The successful growth of such highly ordered...
Galvanostatic charge/discharge curves of the Sb array electrode at a current density of 0.5 A g\(^{-1}\) are displayed in Fig. 2b, which show typical characteristics of Sb electrodes.\(^{25-28}\) In the first discharge curve, it shows the presence of three sodiation plateaus, which are a short slope at 0.590 V, a long plateau at 0.502 V, and a much shorter one at 0.391 V. These three plateaus constantly show in the following curves, corresponding to the sequence of amorphous Sb \(\rightarrow\) amorphous Na\(_3\)Sb \(\rightarrow\) Na\(_3\)Sb(hex)/Na\(_3\)Sb(cub) \(\rightarrow\) Na\(_3\)Sb(hex).\(^{25-28}\) In the first charge curve and the subsequent ones, two pronounced disodiation plateaus are constantly shown, which are a long plateau at 0.800 V and another short one at 0.898 V, corresponding to the process of Na\(_3\)Sb(hex) \(\rightarrow\) amorphous Sb transition and partial crystallization of Sb, respectively.\(^{25-28}\) All of these voltage profiles are in good agreement with the CV results in Fig. 2a. Furthermore, it is worthwhile to emphasize that the voltage profiles of both sodiation and desodiation processes are perfectly reproducible from cycles 1 to 100, indicating the stable structure of Sb nanorod arrays and excellent electrochemical reversibility during cycling.

As shown in Fig. 2c, the Sb nanorod array anode demonstrated excellent cycling performance. At a current density of 0.2 A g\(^{-1}\), it delivered a high capacity of 620 mA h g\(^{-1}\) at the 100th cycle and 521 mA h g\(^{-1}\) at the 250th cycle with a capacity retention of 84%. The cycling performance is comparable to those reported results regarding Sb-based anodes (Table S1, ESI\(^{\dagger}\)). The capacity decay of Sb nanorod arrays was attributed to the inevitable increasing thickness of the SEI film and huge volume changes of the Sb anode upon cycling, as shown in Fig. S3 (ESI\(^{\dagger}\)). The decay can also be accordingly reflected on charge/discharge profiles in different cycles (Fig. S4, ESI\(^{\dagger}\)). It is worthwhile noting that the cycling performance of this anode was obtained without any sophisticated chemical modification of the Sb material. It is reported that the protective coating by carbon or other materials can effectively tolerate the massive volume changes and alleviate the stress–strain during the Na alloying/dealloying reaction.\(^{19,23,24,40}\) Therefore, we deduce that such a strategy could be the direction of further improvement on cycling performance. The areal capacity of Sb nanorod arrays is also calculated, which is about 215 mA h cm\(^{-2}\) at a current density of 80 \(\mu\)A cm\(^{-2}\). The Coulombic efficiency (CE) of the first cycle is around 78.2%, while it stabilizes at around 97.8% for the following cycles, indicating facile and efficient ion and electron transport in this electrode.\(^{31-33}\) When cycled at a large current density of 0.5 A g\(^{-1}\), Sb nanorod arrays showed almost the same capacity with that at 0.2 A g\(^{-1}\), but a shorter cycle life due to more severe morphology changes.

In addition to the high capacity and cyclability, the Sb nanorod array anode also displays remarkably high rate capability. Fig. 2d demonstrates the rate performance investigated at various current densities from 0.1 to 20 A g\(^{-1}\). It is striking to note that the Sb nanorod array electrode still can be reversibly cycled at super high current densities of 10 and 20 A g\(^{-1}\) and deliver large capacities of 579.7 and 557.7 mA h g\(^{-1}\), respectively, indicating the fast transfer of Na ions and electrons through Sb nanorod arrays. When the current densities are reset to 1, 5, and 10 A g\(^{-1}\), the capacities fully recovered and are...
even slightly higher than those of the first set at the same current densities, implying that the unique electrode structure can preserve the integrity of the electrode and accommodate a huge change in the current density, which are highly crucial for high power applications of rechargeable batteries. As far as we know, this is the best rate capability in comparison with the previously reported Sb-based anodes in SIBs, as shown in Table 1. The corresponding voltage profiles of the electrode at various current densities are presented in Fig. 2e. As current density increases from 0.1 to 20 A g\(^{-1}\), the charge/discharge voltage profiles have similar shapes, with a minimal increase of the voltage offset, even at an ultra-high current density of 20 A g\(^{-1}\), suggesting facile electron transport and small mechanical energy loss of the electrode. Moreover, when the current density is reduced back to 1 A g\(^{-1}\) (Fig. S5, ESI\(^{\dagger}\)), the voltage profiles recovered and are perfectly reproducible in comparison with that of the first set at the same current density (1 A g\(^{-1}\)), reflecting the stable structure of Sb nanorod arrays to strongly tolerate the repeated and rapid Na alloying/deloying reactions. Charge working potentials of the electrode at different current densities are shown in Fig. 2f. The potentials display only a small increase of 0.027 V when the current is increased from 0.1 to 1 A g\(^{-1}\), and an increase of 200 times of current brings an increase of the potential of only 0.311 V when the current is increased to 20 A g\(^{-1}\), indicating the excellent structural stability of Sb nanorod arrays and fast electron transport. In addition, the charging times are 6 min 24 s, 3 min 19 s, and 1 min 33 s at current densities of 5, 10, and 20 A g\(^{-1}\), with high charge capacities of 572.4, 579.7, and 557.7 mA h g\(^{-1}\), respectively. The electrodes can be charged and discharged at such high rates with such high capacities in such short time, which is highly desirable for high power and energy devices.

As clearly illustrated in the above results, the highly ordered Sb nanorod array anode shows extremely large capacities, excellent cycle stability, and superior rate capability for Na-ion storage, which can be ascribed to its pathbreaking electrode design on the basis of the following factors. First, the nanoscaled diameter of Sb nanorods can shorten the Na ion diffusion pathway compared to the bulk Sb powders. Nanostructuring of the active materials can also moderate the effect of volume changes and enhance the kinetics of the conversion and alloying reactions.\(^{38-40}\) Second, Sb nanorod arrays themselves as electric conductors directly connect to the conductive Au/Ni substrate offering fast and accessible electron transport, giving rise to superior rate capability. Third, Sb nanorod arrays show good vertical alignment and uniform large interval spacing (about 190 nm), which provide direct channels for the electrolyte and ions to permeate into all the portions of arrays, and thus Na ions can fully contact Sb nanorods without any dead angles, improving Na ion accessibility. This point surpasses the traditional materials including powder-based materials and disordered network in that charge carriers must move through the interstitial regions or spaces within materials to access the internal part. Owing to this feature as well as the large surface area of Sb nanorod arrays, large capacities at high rates are obtained. Moreover, the large interval spacing in arrays can prevent the pulverization by facile strain relaxation during cycling. The third point is extremely significant to ensure Sb nanorod arrays to show high capacities, long-term cycling stability, and excellent rate capability. In order to better reveal the advantages of highly ordered arrays with large interval spacing, we conducted parallel comparative tests between vertically well-aligned Sb nanorod arrays (S-Sb NRs) and attached Sb nanorod arrays (A-Sb NRs) with very limited interval spacing for the permeation of the electrolyte (relating to Na ion transport and strain release) on the electrochemical performance. These two arrays have the same length of 1.5 µm, and more detailed structural parameters of A-Sb NRs can be found in Table S2 (ESI\(^{\dagger}\)).

Fig. 3 demonstrates different Na ion transport modes in these two arrays, noting that Sb metal is a good electric conductor and it can effectively transfer electrons between the conductive substrate and nanorods without the help of conductive additive carbon. As shown in Fig. 3a and b, due to the large interval spacing in vertically well-aligned arrays, Na ions can easily diffuse into the matrix in S-Sb NRs, resulting in superior Na ion accessibility, thus large capacities are highly expected, especially at high current densities. In contrast, the SEM image (Fig. 3c) of A-Sb NRs displays severely agglomerated nanorods and concomitant very limited interval spacing in arrays. Therefore, the electrolyte is very difficult to directly penetrate into the bottom region of A-Sb NRs through the top of attached nanorods (Fig. 3d). As a substitute, Na ions have to diffuse through interstitial regions within arrays, which would lead to incomplete active sites for Na\(^+\), then showing decreased capacities of A-Sb NRs. On the other hand, the large interval spacing in S-Sb NRs can provide a facile strain relaxation during cycling, thereby preventing the pulverization. However, for A-Sb NRs, the joint parts tend to break because of the stress that existed among these entangled Sb nanorods, leading to poor transport of electrons and ions, thereby rapid capacity decay.\(^{41,42}\)

Based on the above analysis of different Na ion transport and strain release modes, we investigated the electrochemical performance of A-Sb NRs and S-Sb NRs under the same testing conditions. As shown in Fig. 4a, the A-Sb NRs have similar CV curves with S-Sb NRs (Fig. 2a), indicating the identical sodiation/desodiation mechanism. However, the capacities and cycling stability are far less than those of S-Sb NRs. In Fig. 4b, A-Sb

![Fig. 3](image-url) SEM images of (a) S-Sb NRs and (c) A-Sb NRs (inset: TEM image of A-Sb NRs). The corresponding schematic illustration of the transport mechanism of Na ions and electrons in (b) S-Sb NRs and (d) A-Sb NRs.
NRs show a first discharge capacity of 529.5 mA h g⁻¹ and a CE of 79.5% at a current density of 1 A g⁻¹. In the following 50 cycles, A-Sb NRs maintain a stable discharge capacity of around 475 mA h g⁻¹, however, the CE gradually decreases, implying that the irreversible reactions occurred during this period. From the 50th cycle, A-Sb NRs undergo rapid capacity decay, delivering only 345.1 mA h g⁻¹ in the 60th cycle. The galvanostatic charge/discharge voltage profiles of A-Sb NRs (Fig. S6, ESI†) further reveal this decay phenomenon from another point of view. In the 50th cycle, the discharge plateau shows a big decrease from 0.37 V in the 10th cycle to 0.17 V and the flat charge plateau at 0.87 is replaced by a big slope. In contrast, an excellent cycling stability of S-Sb NRs is observed at the same current density and the electrode still can retain a constant and even a slightly high capacity of 625.2 mA h g⁻¹ over 60 cycles and a high CE of around 98% (except the first cycle of 83%) (Fig. 4c). Furthermore, the voltage profiles of S-Sb NRs (Fig. S7, ESI†) present perfect reproducibility during 50 cycles. Notably, it is as expected that the capacity, the CE, and the cycling stability of S-Sb NRs are much better than those of A-Sb NRs, which is largely ascribed to more efficient ion transport, as well as more facile strain release in S-Sb NRs.

Nyquist plots of A-Sb NRs and S-Sb NRs are displayed in Fig. 4d and e to investigate their resistance change with increased cycles. From the first cycle to the 50th cycle, A-Sb NRs show a gradually increased resistance (Fig. 4d). However, for S-Sb NRs, the change in resistance is negligible (Fig. 4e), further confirming relatively easier Na ion transport in S-Sb NRs, thereby reducing the irreversible capacity loss and enhancing the cycling performance. For the rate performance of the A-Sb NR electrode (Fig. 4f), it demonstrates a similar trend as S-Sb NRs in the first 45 cycles but with lower capacities. In addition, from the 46th cycle (a current density of 10 A g⁻¹ in the second rate set), the capacities rapidly decrease. Under high current densities, the electrode needs to finish the charge and discharge processes in a very short time. Therefore, high ion accessibility, good electrical conductivity, and stable electrode structure are essential. The A-Sb NR electrode shows limited ion accessibility, and the attached structure of is not conducive to release strain induced by volume expansion, resulting in an unstable electrode structure. As a sum result, under a high current density of 10 A g⁻¹ in the second rate set, the A-Sb NR electrode displays rapid capacity decay. The largely different electrochemical performance between A-Sb NRs and S-Sb NRs fully supports our assumption of the predominance of this highly ordered alignment with a large interval spacing electrode design for Na-ion storage. To more comprehensively reveal the importance of highly ordered arrays with interval spacing, we also compared the electrochemical performance of another two kinds of arrays, as shown in Table S2 and Fig. S8 (ESI†).

In addition, the remarkable electrode integrity is also largely beneficial for the excellent electrochemical performance. The good adhesion between Sb nanorod arrays and the conductive substrate can ensure robust array integrity to accommodate volume expansion/contraction upon cycling, resulting in good cycling and rate performance. To better verify this point, the morphology of Sb nanorod arrays after long-term cycling was also investigated. Fig. 5 shows SEM and TEM images of Sb nanorod arrays cycled at a current density of 10 A g⁻¹ after 70 cycles in the fully desodiation state. As can be seen from the top (Fig. 5a) and side views (Fig. 5b), Sb nanorod arrays still maintain their highly ordered and vertically well-aligned feature with clear interval spacing after long-term cycling at such high current density, which prevents pulverization and preserves electrode integrity, giving rise to excellent cycling and rate performance. We scratched Sb nanorods off the substrate and observed the uniform and well-preserved Sb nanorods on the TEM image (Fig. 5b inset). The diameter and length of the cycled Sb nanorods are around 300 nm and 2.1 μm, respectively, and larger than those of the pristine Sb nanorods (Fig. 1h) with rough surfaces, deriving from the volume expansion/contraction.
Electrochemical performance of a full cell coupled by a P2-Na\textsubscript{2/3}Ni\textsubscript{1/3}Mn\textsubscript{2/3}O\textsubscript{2} cathode and a Sb nanorod array anode was investigated. The structure and electrochemical performance characterization of P2-Na\textsubscript{2/3}Ni\textsubscript{1/3}Mn\textsubscript{2/3}O\textsubscript{2} can be seen in Fig. S9 and Fig. S10 (ESI†). This full cell was tested with a voltage range of 1.4–4.0 V at a large current density of 0.5 A g\textsuperscript{−1} (with respect to the anode weight) using 1.0 M NaClO\textsubscript{4} in EC-PC-5% FEC electrolyte. According to the average working potentials of 3.6 and 0.7 V vs. Na\textsuperscript{+}/Na for the P2-Na\textsubscript{2/3}Ni\textsubscript{1/3}Mn\textsubscript{2/3}O\textsubscript{2} cathode (Fig. S10b, ESI†) and the Sb nanorod array anode (Fig. 2b), respectively, it is reasonably deduced that the full cell operates at around 2.9 V, as indeed shown by Fig. 6a reflecting charge/discharge profiles of the full cell. Fig. 6b shows the cycling performance of this full cell, in which it delivered a superior capacity retention of around 94% before 110 cycles with a capacity of around 620 mAh g\textsuperscript{−1} (relative to Sb anode weight), which is very close to the theoretical capacity of Sb (660 mAh g\textsuperscript{−1}). From the 110th cycle to the 130th cycle, this cell showed a capacity decay to 450 mAh g\textsuperscript{−1}. This decay characteristic is similar to the Na/Sb half cell, due to the inevitable morphology change of Sb (Fig. S3, ESI†). Nevertheless, at such a high current density of 0.5 A g\textsuperscript{−1}, this cell can still work with a high capacity of about 334 mAh g\textsuperscript{−1} up to 250 cycles and an extremely stable CE of around 98%. Although the capacity of the 250th cycle is only 54% of the 110th capacity, the value of 334 mAh g\textsuperscript{−1} is very attractive considering such a large current density of 0.5 A g\textsuperscript{−1}. Moreover, according to the above studies, the cycling stability of this full cell might be better at a lower current density.

Notably, this full cell also displayed high rate capability, as shown in Fig. 6c. Benefiting from the great rate capability of the Na/Sb half cell, it can be cycled at very large current densities of 10 and 20 A g\textsuperscript{−1}, and maintained a stable reversibility. In addition, these capacities can be fully recovered when the cell went back to the low current densities. The energy density and the power density of the full cell were further evaluated with a Ragone plot, which were calculated based on the total mass of the cathode and anode active materials, as shown in Fig. 6d. These values show a clear comparison with commercial lithium-ion batteries and electrochemical capacitors. Such a cell could provide much higher power densities than commercial Li-ion batteries, while the energy densities are several times bigger than those of electrochemical capacitors. These capabilities suggest that Sb nanorod array anodes can be used to build large energy storage and conversion devices with both high-power and high-energy densities.

4. Conclusions

In summary, we presented large-scale highly ordered Sb nanorod arrays with uniform large interval spacing. Used as a SIB anode, Sb nanorod arrays delivered a high capacity retention of 84% up to 250 cycles. Remarkably, the anode showed superior rate capability with high capacities of 579.7 and 557.7 mA h g\textsuperscript{−1} at 10 and 20 A g\textsuperscript{−1}, respectively, and fully recovered the low rate capacities. The excellent electrochemical performance is achieved in return for its pathbreaking electrode design which ensures high Na ion accessibility, fast electron transport, and strong structural integrity. Moreover, the successful application of such a full cell indicates that Sb nanorod array anodes can be used to build large energy storage and conversion devices with both high-power and high-energy densities.

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Notes and references


15. Z. Zhan and Y. Lei, ACS Nano, 2014, 8, 3862–3868.


