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A type of sodium-ion full-cell with layered $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ cathode and pre-sodiated hard carbon anode

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A new structure of sodium-ion full-cell with layered $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ cathode and pre-sodiated hard carbon anode is reported. The pre-sodiation of hard carbon anode, achieved via a facile approach in a three-electrode battery, can significantly enhance the initial coulombic efficiency of sodium-ion full-cell. As a consequence, a much higher capacity is obtain in the hard carbon/ $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ sodium-ion battery. Based on the cathode mass, the full-cell with pre-sodiated hard carbon anode can exhibit a reversible capacity of 93 mAh g⁻¹.

Lithium-ion batteries are widely applied in portable electronic products and considered as the best candidates for electric vehicles and hybrid electric vehicles in decades.¹⁻³ However, mass production of lithium-ion batteries is hindered by cost and the shortage of lithium resources. In sharp contrast to lithium, abundant sodium resources offer an economic potential in energy storage. Therefore, room-temperature sodium-ion batteries have attracted much attention as large-scale energy storage devices in recent years.⁴⁻⁶

To develop sodium-ion batteries, novel design of electrodes is still urgent. For anodes in sodium-ion batteries, most works focused on hard carbon materials due to their large interlayer distance and disordered structure, which can facilitates sodium-ion insertion-extraction.⁷⁻¹⁵ Typical cathode materials are more variety compared with anode materials such as polyanions and layered transition-metal oxides.¹³⁻²⁰ More recently, layered $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ was proposed as cathode material which exhibited promising charge-discharge curves in metal sodium half-cell.²¹ However, to the best of our knowledge, there is no literature reported on the performance of layered $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ in sodium-ion full-cell, which is important for its further application.

For the first time, we reported a sodium-ion full-cell in couple between hard carbon anode and $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ cathode.

Moreover, it is well known that cathode materials are hard to complete full charge due to the solid electrolyte interphase (SEI) layer forming on anode surface, mainly leading to a low coulombic efficiency, and the initial instable SEI always results in a poor cycle life.^{15, 22} In order to address these issues, lithium pre-doping strategy was widely used in lithium-ion batteries and lithium-ion hybrid capacitors.²³⁻²⁵ Based on this, for the first time, we employed sodium pre-doping strategy in assembled sodium-ion full-cell. As presented in the schematic structure in Fig. 1, a metal sodium foil was used as an extra sodium source and separated by a separator to produce a three-electrode battery. Therefore, sodiated hard carbon can be achieved during discharge process (sodium-ions insertion) for the metal sodium/hard carbon half-cell. The electrochemical performance of the sodium pre-doping hard carbon/ $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ sodium-ion full-cell then can be evaluated, and significantly enhanced capacity is obtained.

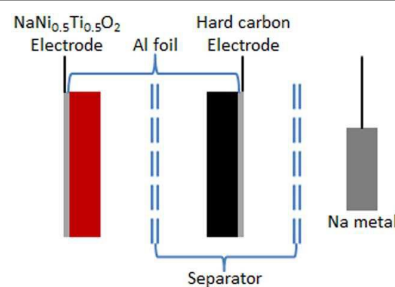


Fig. 1 Schematic structure of three-electrode sodium-ion battery.

The XRD pattern of as-prepared $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ sample was shown in Fig.2. All of the diffraction peaks (black lines) can be indexed to R-3m space group with the $\alpha\text{-NaFeO}_2$ structure apart from trace impurity of NiO (marked with *), consistent with reported literature.²¹ Rietveld refinement is conducted in order to calculate the lattice parameters of as-prepared layered $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ material. It is obvious that calculated XRD patterns from the refined profile (red dots) are well agreement with the experimental data, which the refine lattice parameters are $a = b = 3.3003(6) \text{ \AA}$ and $c = 16.1410(2) \text{ \AA}$.

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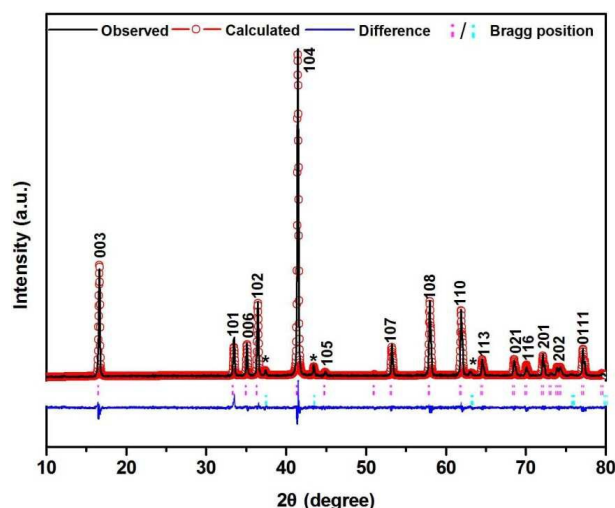


Fig. 2 Rietveld refined XRD pattern of as-prepared $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ sample with experimental data (black line), calculated profile (red dots), difference curve (blue line), and allowed Bragg reflections (vertical magenta and cyan bars). The NiO phase is marked with asterisk signs.

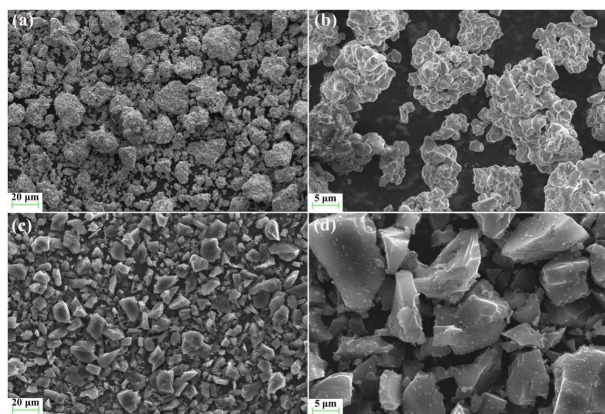


Fig. 3 SEM images of as-prepared $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ sample (a, b) and commercial hard carbon material (c, d).

SEM images shown in Fig. 3 demonstrated the morphologies of as-prepared $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ sample and commercial hard carbon material. The as-prepared $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ sample is composed with agglomerate primary particles and form large micro-sized second particle (Fig. 3a and 3b). For the commercial hard carbon showed in Fig.3c and 3d, it is an irregular bulk material.

Electrochemical performance of $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ cathode and hard carbon anode in sodium-ion half-cells at room temperature are evaluated, shown in Fig. 4a and 4b. $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ electrode delivers a reversible capacity of 109 mAh g^{-1} when cycled between 4.1 V and 2.0 V vs. Na/Na^+ at a current of 10 mA g^{-1} , and the coulombic efficiency of the first cycle is 85.5%, as shown in Fig. 4a. In addition, the initial three charge-discharge curves overlap well, indicating an excellent reversible sodium-ion insertion-extraction behavior. Hard carbon electrode exhibits a reversible capacity of 230 mAh g^{-1}

at a current of 20 mA g^{-1} as shown in Fig.4b, and the initial coulombic efficiency is 83.8%. The initial irreversible capacity is about 45 mAh g^{-1} due to the formation of SEI on hard carbon electrode surfaces, which consists of mainly inorganic species in sodium-ion batteries.²⁶ Fig. 4c is the first charge-discharge curve of the hard carbon/ $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ sodium-ion full-cell. The initial coulombic efficiency is 64.7% with a specific capacity of 82 mAh g^{-1} based on cathode active material when testing between 4.0 V and 1.5 V at a current of 10 mA g^{-1} . Considering the obvious irreversibility in the first cycle, we adopted a three-electrode pouch cell as mentioned in Fig.1 to pre-dope sodium-ions into the anode electrode. The sodium pre-doping was conducted by electrochemical discharge process of hard carbon anode using the metal sodium foil as counter electrode. The current density for pre-sodiation is 10 mA g^{-1} , and the discharge capacity is approximately 45 mAh g^{-1} . Typical voltage profile of pre-sodiation process for hard carbon anode is displayed in the inset of Fig. 4c. The first cycle voltage curve for the pre-sodiated hard carbon/ $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ full-cell is also demonstrated in Fig.4c. In contrast, the initial coulombic efficiency is enhanced to 73.0% with a specific capacity of 93 mAh g^{-1} based on cathode mass. The pre-sodiated full-cell shows improved capacity. After the first charge-discharge cycle at a current of 10 mA g^{-1} , the cycle performance is also much improved, as the corresponding capacities retentions are 72.0% and 69.5% after 100 cycles for with and without pre-sodiated full-cells, respectively. The improved cycle performance may originate from more stable surface passivation layer including SEI forming on carbon electrode surface in the pre-sodiated hard carbon/ $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ full-cell during the first cycle, which can be ascribed to the fact that pre-doping process is an effective scavenger for moisture in the system.²³ Further work on the optimization of the $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ sample and development of high performance sodium-ion battery will be carried out in the near future.

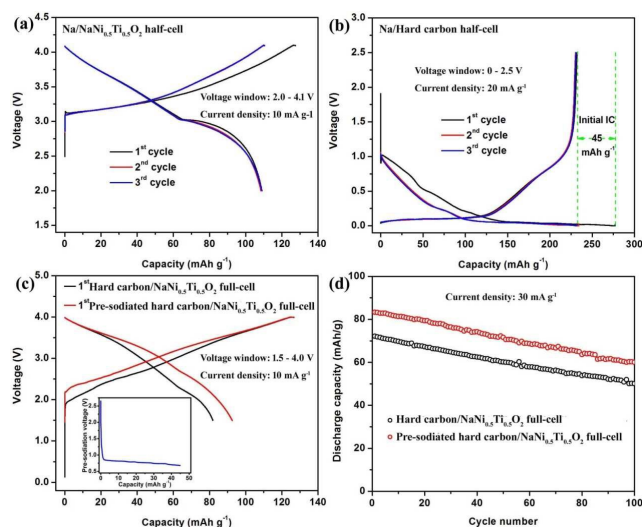


Fig. 4 (a, b) Initial three charge-discharge profiles of $\text{Na}/\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ and $\text{Na}/\text{Hard carbon}$ half-cells, respectively, and (c, d) first cycle and cycle performance of hard carbon/ $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ full-cells with and without pre-sodiation. The inset is typical voltage profile of pre-sodiated process for hard carbon anode.

In summary, a novel type of sodium-ion full-cell constructed with $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ cathode and pre-sodiated hard carbon anode is investigated. The pre-doping of sodium ions can be realized via a three-electrode structure battery, in which metal sodium foil was placed behind carbon anode and sodiation process was complete by electrochemical sodium intercalation anode using the sodium foil as counter electrode. After coupling with $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ cathode, the full-cell delivered a higher capacity and cycle stability in comparison with conventional hard carbon/ $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ sodium-ion battery. At a current of 10 mA g^{-1} , the battery consisting of $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ cathode and pre-sodiated hard carbon anode can exhibit a reversible capacity of 93 mAh g^{-1} based on cathode mass, while it is only 82 mAh g^{-1} without pre-sodiation process.

Experimental Section

Materials: TiO_2 powder was obtained from Shanghai Pengbo Titanium Dioxide Co. Ltd., China. Hard carbon material was purchased from Kureha Co., Japan. All other chemicals were used directly without further purification.

Preparation of $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$: A conventional high-temperature synthetic approach is employed to prepare $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ sample. First, 1.20 g of TiO_2 powder was dispersed in 50 mL distilled water under ultrasonication at room temperature for 1 h . 4.37 g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 1.67 g Na_2CO_3 (5% excess condition) were added to the suspension under magnetic stirring. After it turns to a uniform sticky suspension, the mixture was transferred to an oven at $80 \text{ }^\circ\text{C}$ to evaporate the water. Then, the mixture was ground, heated in air to $900 \text{ }^\circ\text{C}$ in a muffle furnace for 12 h , and transferred to an argon-filled chamber before cooling to $200 \text{ }^\circ\text{C}$. Finally, dark-green powder was obtained, sieved by a 200-mesh screen and used in all the electrochemical and structural studies.

Characterization: Power X-ray diffraction (XRD) was carried out on a Rigaku Mini-Flex600X-ray diffractometer using $\text{Cu-K}\alpha$ radiation. Data was collected over the range $10^\circ \leq 2\theta \leq 80^\circ$ at a scanning rate of 2° min^{-1} . Rietveld refinement of the diffraction pattern was performed with the RIETAN-2000 program. The morphologies of sample were investigated by a ZEISS EVO-18 scanning electron microscope (SEM).

Electrochemical measurements: All the electrodes were prepared by a doctor-blade casting process. The $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ electrode consists of $80 \text{ wt.}\%$ active material, $12 \text{ wt.}\%$ Super P, and $8 \text{ wt.}\%$ polyvinylidene fluoride (PVDF). The hard carbon electrode contains $94 \text{ wt.}\%$ active material, $1 \text{ wt.}\%$ Super P, and $5 \text{ wt.}\%$ PVDF. The current collectors for cathode and anode electrodes are both metal aluminum foil. The electrodes were dried thoroughly and punched into suitable size. In the metal sodium half-cells, circular disks having a diameter of 12 mm were carried out for CR2025 cells testing. In the sodium-ion full-cells, squares with $30 \text{ mm} \times 30 \text{ mm}$ were performed to fabricate pouch cell and the anode to cathode capacity loading

ratio was $1.08:1$. A 1.0 M solution of NaClO_4 in propylene carbonate was used as the electrolyte and a glass fiber was used as the separator. Electrochemical evaluation was performed on a Land CT2001A cell testing instrument.

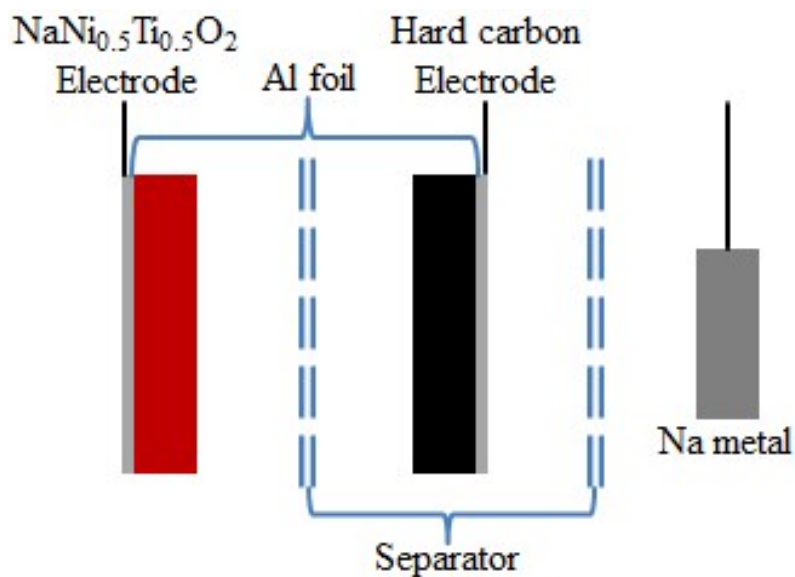
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Graphical Abstracts



A new type of sodium-ion full battery consisting of $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ cathode and pre-sodiated hard carbon anode is reported. The pre-sodiation can be achieved via a three-electrode cell design, and a higher capacity and coulombic efficiency is obtained for the hard carbon/ $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ full battery.