Supporting Information

Exploration of Na$_{2.65}$Ti$_{3.35}$Fe$_{0.65}$O$_9$ as anode materials for Na-ion batteries

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Fig. S1. TGA of precursor of Na$_{2.65}$Ti$_{3.35}$Fe$_{0.65}$O$_9$

The thermal properties of the obtained Na$_{2.65}$Ti$_{3.35}$Fe$_{0.65}$O$_9$ precursor were studied using TG analysis. Fig. S1 displays the TG curve for the Na$_{2.65}$Ti$_{3.35}$Fe$_{0.65}$O$_9$ precursor. It shows a first weight loss around 400$^\circ$C, which is attributed to the evaporation of residual water and the removal of chemically bound water in the sample. The following sharp drop in weight above 700 $^\circ$C corresponds to the decomposition of raw materials and the formation of Na$_{2.65}$Ti$_{3.35}$Fe$_{0.65}$O$_9$ phase. The weight loss between 700 and 900$^\circ$C is very little. This behavior implies that the formation of Na$_{2.65}$Ti$_{3.35}$Fe$_{0.65}$O$_9$ phase is completed at this stage. So, the samples were annealed at 750 $^\circ$C, 800 $^\circ$C, 850 $^\circ$C and 900 $^\circ$C in this work.
The XRD patterns of the as-synthesized samples display in Fig.S2. The results suggested that the Na$_{2.65}$Ti$_{3.35}$Fe$_{0.65}$O$_9$ has been formed after sintering at 700 °C, and with the increasing of sintering temperature, the crystallinity of the samples increased. It is clearly that the main diffraction peaks positions of the materials obtained at 800 °C agree well with Na$_{2.65}$Ti$_{3.35}$Fe$_{0.65}$O$_9$ (PDF No.04-014-0704). However, there are still weak impurity peaks at 21.5° and 30°, it showed that the obtained product at 800 °C still contains trace amounts of impurities. After sintering at 850 °C and 900 °C, the XRD results (Fig.S2c and d) are in good agreement with isostructural Na$_{2.1}$Ru$_4$O$_9$, suggesting the formation of monoclinic phase crystal.
Fig. S3. SEM of the samples obtained at different temperature: (a) 750 °C, (b) 800 °C, (c) 850 °C and (d) 900 °C for 15h.

Fig. S3 shows SEM images of the four samples obtained at different temperatures. It can be observed that Na\(_{2.65}\)Ti\(_{3.35}\)Fe\(_{0.65}\)O\(_9\) with rods morphology has begun to form at 800 °C; When sintering temperature increase to 850 °C, more uniform rods can be obtained. With the further increase of temperature, rods become blocks (Fig. S3d).

![Fig.S4. EDS-element distribution mapping images of Na\(_{2.65}\)Ti\(_{3.35}\)Fe\(_{0.65}\)O\(_9\)/C.](image)

The elemental mapping of carbon (Fig. S4(A)) by EDS clearly show that carbon was homogeneously distributed around the Na\(_{2.65}\)Ti\(_{3.35}\)Fe\(_{0.65}\)O\(_9\) microcrystallites. The EDS elemental mapping results for other elements in the same area are shown in Fig. S4B–E. Although the carbon coating greatly contributed to the excellent rate capability of the Na\(_{2.65}\)Ti\(_{3.35}\)Fe\(_{0.65}\)O\(_9\) electrode, the carbon coating effect was not significant at a low current rate which typically represents the intrinsic electrochemical performance of new cathode materials.
Fig. S5. Structural stability of Na$_{2.65}$Ti$_{3.35}$Fe$_{0.65}$O$_9$ upon cycling

The difference between XRD patterns of the pristine electrode and the sample in the discharged state after 20 cycles with a 0.5 C cycling rate was insignificant (Fig. S5), indicating good structural stability during charging/discharging. This implies that Na$^+$ ions are immobile in the structure and do not significantly affect the structural evolution upon cycling.