

Supporting Information

Molten Salt Electrochemical Synthesis of Sodium Titanates as High Performance Anode Materials for Sodium Ion Batteries

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In order to elucidate the correlations between the potential of cyclic voltammograms (CVs) in three-electrode system and the voltage of electrolysis in two-electrode system, the decomposition voltage of salts (NaF-NaCl-NaI) were carefully measured. Typically, in the molten salts system, an iron wire and a graphite crucible were used as work electrode and counter electrode, respectively. The stable current (after ~ 5 minutes of the beginning of applied voltage) was recorded at different voltages (0.5 V, 1.0 V, 1.2 V, 1.5 V, 1.8 V, 2.0 V, 2.3 V, 2.5 V, 2.8 V, 3.0 V, 3.3 V). The results are shown in Fig. S1.

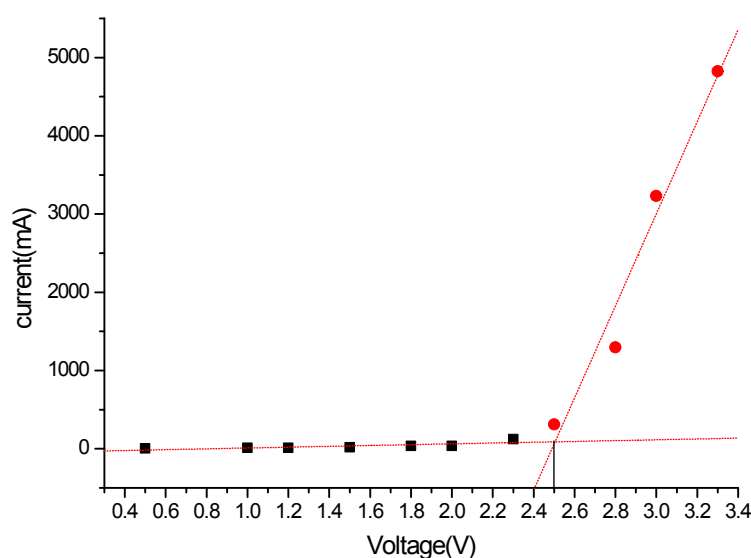


Fig. S1 The current-voltage correlations of molten salts of NaF-NaCl-NaI at 600 °C in electrolytic cell with two electrodes .

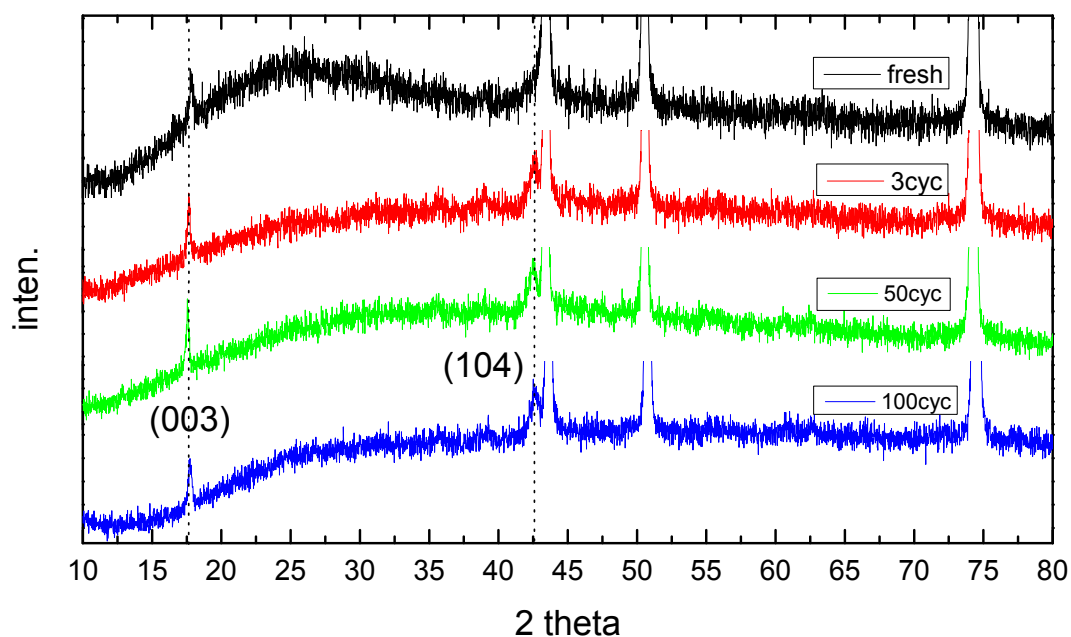


Fig. S2 Ex-situ XRD patterns of the $\text{Na}_{0.46}\text{TiO}_2@\text{C}$ electrodes and the corresponding charge-discharge cycle numbers (before cycling, after 3 cycles, after 50 cycles, and after 100 cycles) at current density of 100 mA g^{-1} . The three strong peaks at 43.3° , 50.4° and 74.1° are from the Cu foil current collector.

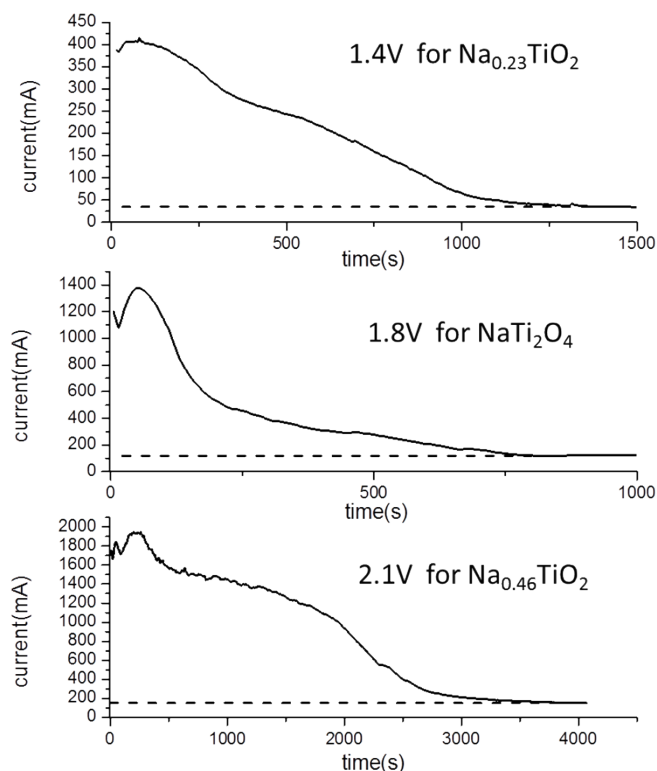


Fig. S3 Current-time curves recorded during electrolysis of solid TiO_2 in molten NaF-NaCl-NaI at 600°C with the applied voltage of (a) 1.4, (b) 1.8, and (c) 2.1 V. The horizontal dotted lines are used for subtracting the background current.

Table S1 the crystal lattice parameters of all compounds

	Anatase TiO ₂	Rutile TiO ₂	Na _{0.23} TiO ₂	Na _{0.46} TiO ₂	NaTi ₂ O ₄
structure	Tetragonal	Tetragonal	Monoclinic	Hexagonal	Orthorhombic
lattice parameters	3.7852 3.7852 9.6139 90×90×90	4.5933 4.5933 2.9592 90×90×90	15.159 3.844 6.464 90×106.9×90	2.958, 2.958, 15.41 90×90×120	9.269, 10752, 2.9562 90×90×90

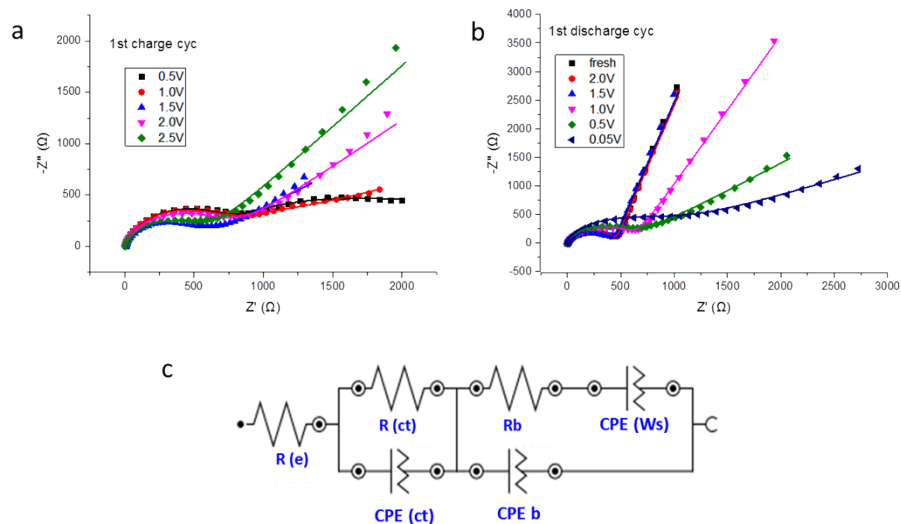


Fig. S4 Nyquist plots of the Na_{0.46}TiO₂@C electrodes in the first cycle (a) charge process and (b) discharge process at 100 mA g⁻¹, obtained by applying a sine wave with amplitude of 10 mV in the frequency from 0.1 Hz to 100 kHz. Figure c is corresponding equivalent electrical circuit for fitting the data.

Table S2 Impedance parameters of Na_{0.46}TiO₂@C electrodes in the first cycle at different state of charge and discharge with current density of 100 mA g⁻¹ (Na as counter electrode). The values above 1.5V are only for reference.

parameters						
first charge cycle	2.5V	2.0V	1.5V	1.0V	0.5V	
R _(e) (Ω)	3.56	2.74	8.4	2.20	2.20	
R _(ct) (Ω)	554	682	464	693	747	
first discharge cycle	OCV(~2.8V)	2.0V	1.5V	1.0V	0.5V	0.05V
R _(e) (Ω)	1.91	2.43	2.04	1.71	1.12	2.61
R _(ct) (Ω)	456	461	439	649	616	649