Sodium ion battery energy density

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Another obvious path to increase the specific energy of NVPF consists in harnessing the remaining sodium ($Na_1V_2(PO_4)_2F_3$-$Na_0V_2(PO_4)_2F_3$) at high potential so as to reach theoretical energy densities of ~800 Wh kg-1. A significant amount of research effort has been directed toward this goal, but have remained unproductive in accordance with density functional theory calculations stating that the removal of the third sodium ion should occur at potential (>4.9 V) that is too high for present electrolytes18,19. The accessibility of the third sodium ion in NVPF was thus remaining an open question.

Inadvertently, in our search toward exploring better electrolytes for the NVPF/C sodium ion system20 we observed, by prolonged charging time at high potential, the feasibility to modify the voltage-composition profile of the charge/discharge curve (e.g smoothing of the voltage features), hence providing a hint of some sodium electrochemical activity at high potential (Supplementary Figure 1). This inspired us to undertake a deeper exploration of $Na_3V_2(PO_4)_2F_3$ oxidation at high voltage.

Here in this work, we demonstrate the feasibility to electrochemically remove nearly three sodium ions upon oxidation till 4.8 V vs Na^+/Na^0 with the concomitant formation of a new disordered "NVPF" phase that can reversibly uptake and release around three sodium ions on the following cycle; two between 4.2 and 3.6 V and the last one at 1.6 V. This provides a 20% gain in specific energy for NVPF/C sodium ion cells. We also demonstrate the benefits of the low voltage plateau to secure the use and the storage of such cells down to zero volts, and the feasibility of monitoring the state of charge (SoC) thanks to the S-shape profile of the voltage-composition curves. Our findings offer unprecedented insight into the development of highly performing sodium ion systems.

Electrochemical characterization of NVPF samples in NVPF/Na half cells at a current of C/10 and cycled between 4.4 and 3.0 V. The first charge process alone is controlled by limiting the amount of Na^+ extracted (Dx = 2.0, 2.25, 2.50, 2.75, and 3.0). a Voltage-composition curves (left) and their corresponding dQ/dV curves (right). b The corresponding capacity retention plots

Electrochemical characterization of NVPF samples in NVPF/Na half cells cycled between 4.4 and 1.0 V. a First cycle activation in which the charging potential is used up to 4.8 V and charge process controlled by limiting the Dx (Na) = 2.0, 2.25, 2.50, 2.75, and 3.0 extracted, followed by discharge to 1 V at C/10. The inset shows the amount of Na^+ extracted at ~4.75 V and reinserted at ~1.6 V. b The charge-discharge profile of the subsequent second cycle in the voltage window of 4.4 and 1.0 V. c The corresponding capacity retention plots

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Galvanostatic intermittent titration-technique (GITT) test of NVPF-2.75 sample after the first formation cycle. The cell was cycled at C/10 rate and the relaxation time was controlled either by 4 h or by limiting dV/dt < 0.1 mV/s; The red and blue solid lines show the experimental GITT curve on charge and discharge respectively, with the black dashed line showing the equilibrium potential after each relaxation process. The red and blue filled circles represent the Ohmic resistance at each point on charge and discharge process respectively. The inset shows NVPF-2.75/Na cell cycled at C/10, C/100, and C/500 within the range of voltage drop during the first discharge process

Structural evolutions during three sodium ions extraction/insertion in NVPF. a Synchrotron X-ray diffraction patterns of the charged samples with different amounts of Na extracted (NVPF-2.0, NVPF-2.25, NVPF-2.5, NVPF-2.75, and NVPF-3.0). b The other set of samples further discharged down to 1 V

V-F bond lengths and sodium distribution within the structure of NVPF samples. Structures of NVPF samples, from left to right: pristine, NVPF-2.0, NVPF-3.0, NVPF-2.75 discharged to 3.0 V, and NVPF-2.75 discharged to 1.0 V. Top: view of the VO8F3 bioctahedra with relevant V-F bond lengths and the average V-O/F distances labeled as <d>; bottom: distribution of Na atoms within the structure. For each composition, the space group is indicated. V is blue, O is red, F is gray, Na is yellow, and Na vacancies are milky white

NMR spectroscopic evidence of sodium disorder in NVPF. a-e 23Na and f-j 31P magic angle spinning-nuclear magnetic resonance spectra after a Hahn echo sequence recorded at 4.7 T and a spinning rate of 50 kHz. a, f Pristine NVPF. b, g NVPF-2.5. c, h NVPF-3.0 discharged to 3.0 V. d, i NVPF-3.0 discharged to 3.0 V and 1.0 V respectively. e, j NVPF-2.0 discharged to 1.0 V. The stars indicate spinning sidebands, the red arrow shows a small contribution from neighboring V4+ ions in the pristine NVPF. The dashed lines are guide for the eyes. The 23Na spectra are shown without modification, while the 31P spectra levels were adjusted for clarity

Evolution of the vanadium oxidation state upon Na+ extraction/insertion. a The voltage-composition curve of NVPF-3.0 sample cycled at C/10 in which the experimental points used for ex situ X-ray absorption analysis are marked with the respective Na-stoichiometry. The normalized (b) V L-edge and c O K-edge X-ray absorption spectra of the corresponding charge (left) and discharge (right) samples obtained in total fluorescence yield mode

Electrochemical performance of NVPF/C full cells. The voltage-composition curves a and cycling performance b of NVPF/C full cell of NVPF-2.0, 2.25, 2.5, 2.75, and 3.0 samples cycled between 4.3 and 2.0 V after first activation process up to 4.8 V at C/10 followed a potentiostatic charging until reaching the exact amount of Na+ content, where insets in b is the histogram of the discharge energy density based on the mass of NVPF. c The voltage-composition curves of NVPF/C full cell of NVPF-2.0, 2.25, 2.5, 2.75, and 3.0 sample cycled down to 0 V with the inset showing the histogram of energy density based on the mass of NVPF. d The cycling performance of NVPF-2.0 and NVPF-2.75 in a full cell before and after zero volt over-discharge tests for 1 week

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