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Tunable lithium storage properties of metal lithium titanates by stoichiometric modulation

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A simple stoichiometric modulation of Na₂−xSr₂Li2Ti6O14 was developed to achieve tunable electrochemical properties of the material. The concept was confirmed experimentally and theoretically using density functional theory (DFT) calculations. Both the operating potential and the amount of reversibly intercalated lithium ions were manipulated by simply changing the Na/Sr ratio. These unique characteristics originated from a gradual change in the electron density on the Ti atoms and the extra lithium insertion sites at SrLi2Ti6O14. As a promising anode material for lithium-ion batteries, Na₂−xSr₂Li2Ti6O14 was developed to achieve tunable electrochemical properties and excellent performance.

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1. Introduction

Precise control of applied potential is an important technique during the operation of electronic devices (e.g., OLEDs) due to its direct association with the overall efficiency [1,2]. However, battery systems cannot always satisfy the optimized potentials of every device because the output potential of batteries is always fixed. Therefore, the tunability of the operating potential of battery systems at the material level is highly desirable. However, strategies for adjusting the electrochemical properties of materials have rarely been reported due to the general assumption that the intrinsic property of these materials cannot be easily adjusted.

As a promising anode material for Li-ion batteries (LIBs), MLi2Ti6O14 (MLTO, M = 2 Na, Sr, Ca, Ba and Pb) has been investigated with a focus on enhancement of its electrochemical performance for MLTOs containing single M species [3–11]. Previous studies have revealed that all of the MLTOs are constructed upon the same TiO6 octahedral arrangements, which suggests the possibility of MLTO’s preparation with two or more M species in the same material. Because the electrochemical properties of MLTO vary with the M species [12–16], MLTO with different electrochemical properties can be expected by merging two types of MLTOs.

The operating potential of titanate-based compounds is determined by the Ti³⁺/Ti⁴⁺ redox energy [17]. The energy depends on the types of neighboring atoms and their relative positions with respect to Ti atom. Therefore, based on their species and stoichiometric combinations, M atoms can be employed to tune the MLTO operating potential. Moreover, an extra lithium insertion site is available in certain M species. Due to the characteristics of MLTOs, various operating potentials and gravimetric capacities can be achieved by controlling the stoichiometry of the M atoms.

Herein, we report the preparation of MLTOs with two co-existing M species for application as an anode material of LIBs. Utilizing the equivalent crystal structures of MLTOs, gradual modulation of the electrochemical properties is possible by controlling the M atom composition. To prove our concept, MLTO containing both sodium and strontium (Na₂−xSr₂Li2Ti6O14, NaSrLTO) was employed, and the M species stoichiometry was controlled. The operating potential and equivalent amounts of reversibly intercalated lithium ions gradually changed as the Sr/Na ratio was modulated.

2. Experimental

Na₂−xSr₂Li2Ti6O14 samples were prepared from CH₃CO₂Na:3H₂O, (CH₃CO₂)₂Sr:0.5H₂O, CH₃CO₂Li:2H₂O, TiO₂ and oxalic acid (CH₃CO₂Na: (CH₃CO₂)₂Sr:CH₃CO₂Li:TiO₂: oxalic acid = 2 – 2x: x: 2: 6: 2, x = 0, 0.25, 0.5, 0.75, 1). The powder was calcined in air at 1000 °C for 24 h to obtain the Na₂−xSr₂Li2Ti6O14 samples that are 1–10 μm in size. Electrochemical measurements were carried out using CR2032-type coin cells at room temperature (25 °C). The electrodes were fabricated with the active material, Super P and poly(vinylidene difluoride) (PVdF) at a weight ratio of 8:1:1. These three components were mixed...
with N-methylpyrrolidone (NMP) and cast on Cu foil using a doctorblade with an active material loading of ≈1 mg/cm². The electrode was dried under vacuum at 120 °C for 12 h. A porous polypropylene film and 1.15 M LiPF₆ in an EC:EMC:DEC = 3:5:2 solvent were used for the separator and electrolyte, respectively. Galvanostatic charge/discharge tests were performed with a multichannel automatic battery cycler (WonATech, WBCS3000). DFT calculations using the Vienna ab initio simulation package code were employed to calculate the formation energies and Bader charge of Ti atoms in the crystal structure [18]. The details of the characterizations and DFT calculations have been described in a previous study [19].

### 3. Results and discussion

Fig. 1a shows the X-ray diffraction (XRD) patterns of NaSrLTOs. The patterns for Na₂₂Li₂Ti₆O₁₄ (NaLTO) and Sr₂₂Li₂Ti₆O₁₄ (SrLTO) were in good agreement with those from previous studies on MLTOs [7,12,13]. These two samples exhibit similar patterns because NaLTO and SrLTO have analogous crystal structures. However, as shown in the magnified peak between 10° and 15°, the minor peaks corresponding to SrLTO gradually appeared with increasing Sr content. The difference in the peak between 10° and 15°, the minor peaks corresponding to SrLTO derive from the different lattice constants of NaLTO and SrLTO. Never-theless, the main oxidation peaks gradually shifted to a higher potential as the Sr content increased. In addition, the shoulder peak, which corresponds to the additional peak for SrLTO at 1.15 V, gradually faded as the Sr content increased.

The changes in the operating potential with NaSrLTOs originated from the atomic structure of MLTO. Fig. 3a shows the octahedral TiO₆ frameworks of NaSrLTOs, and the M atoms are located in the 8f Wyckoff positions. In NaLTO, the 8f Wyckoff position was fully occupied by two Na atoms, and this position in SrLTO was half occupied by one Sr atom. The similarity of the crystal structures of NaLTO and SrLTO results in substitution of 2 equivalent Na atoms to 1 equivalent Sr atom. By a gradual exchange of Na atoms with Sr atoms, the operating potential gradually increased from 1.25 V to 1.4 V due to the gradual change in the Ti³⁺/Ti⁴⁺ redox reaction. Fig. 3b shows the differential charge density map near the Ti atoms. After the Na atoms were substituted by Sr atoms, the electron density near the Ti atoms decreased. Therefore, the amount of reversibly intercalated lithium ions increased linearly. Fig. 2b shows the rate capability test results. The samples with a higher Sr content exhibited better rate capability due to the higher electrical conductivity of SrLTO compared to that of NaLTO [12]. In long-term cycle tests at 200 mAh g⁻¹, all of the NaSrLTO samples exhibited a capacity retention in excess of 99% after 100 cycles (data are not shown).

The differential capacity analyses of the charge curve at 10 mA g⁻¹ demonstrated a shift in the potential plateau of NaSrLTOs (Fig. 2c). For NaLTO, an oxidation peak appeared at 1.27 V. However, the peaks for SrLTO were primarily located at 1.42 V and 1.15 V, which corresponds to two distinctive potential plateaus for SrLTO. The peak positions of NaSrLTOs are broader than those of NaLTO and SrLTO. The decrease in the sensitivity of the potential is due to distortion of the crystal structure derived from the different lattice constants of NaLTO and SrLTO. Nevertheless, the main oxidation peaks gradually shifted to a higher potential as the Sr content increased. In addition, the shoulder peak, which corresponds to the additional peak for SrLTO at 1.15 V, gradually faded as the Sr content decreased.

### Table 1

<table>
<thead>
<tr>
<th>Composition</th>
<th>Total energy (eV)</th>
<th>Formation energy (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂₂Li₂Ti₆O₁₄</td>
<td>−1.21 × 10³</td>
<td>0.00</td>
</tr>
<tr>
<td>Na₁₂Sr₂₂Li₂Ti₆O₁₄</td>
<td>−1.21 × 10³</td>
<td>−16.2</td>
</tr>
<tr>
<td>NaSr₂₂Li₂Ti₆O₁₄</td>
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<td>−19.9</td>
</tr>
<tr>
<td>Na₈Sr₁₅Li₂₂Ti₆O₁₄</td>
<td>−1.15 × 10³</td>
<td>−7.25</td>
</tr>
<tr>
<td>Sr₂₂Li₂Ti₆O₁₄</td>
<td>−1.12 × 10³</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Fig. 1. XRD patterns of Na₂₋ₓSrₓLi₂Ti₆O₁₄ from (a) experimental and (b) simulated data. The peaks in the magnified XRD patterns between 10° and 15° correspond to the {111} plane of Sr₂₂Ti₂O₁₄.
Fig. 2. (a) Galvanostatic charge/discharge profiles of Na$_{2-2x}$Sr$_x$Li$_2$Ti$_6$O$_{14}$ at a current density of 10 mA g$^{-1}$. (b) Rate capability results of Na$_{2-2x}$Sr$_x$Li$_2$Ti$_6$O$_{14}$ from 10 mA g$^{-1}$ to 1000 mA g$^{-1}$, for 5 cycles each. (c) Differential capacity analyses of charging profiles in 10 mA g$^{-1}$ of Na$_{2-2x}$Sr$_x$Li$_2$Ti$_6$O$_{14}$.

Fig. 3. (a) Crystal structures of Na$_2$Li$_2$Ti$_6$O$_{14}$, NaSr$_{0.5}$Li$_2$Ti$_6$O$_{14}$ and SrLi$_2$Ti$_6$O$_{14}$. The red circle indicates the 8$f$ Wyckoff position of Na$_{2-2x}$Sr$_x$Li$_2$Ti$_6$O$_{14}$. (b) Differential charge densities near Ti atoms (shown as a white circle in Fig. 3a) constituting Na$_2$Li$_2$Ti$_6$O$_{14}$ and SrLi$_2$Ti$_6$O$_{14}$. The yellow color indicates a loss of electrons, and blue represents a gain of electrons. The isosurface levels of the two images are $1 \times 10^{-3}$ e a$_0^{-3}$.

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the charge on the Ti atoms in SrLTO becomes more positive. The quantified charges on the Ti atoms were obtained in the form of Bader charges (Fig. 3c). The Bader charge was calculated from the sum over the differential charge densities near the Ti atom. Consequently, the Bader charge of a Ti atom increased as the Sr content increased. Because the Ti atoms acquire more ionic characteristcs under a Sr-rich condition, the interaction between the inserted Li and active materials becomes stronger [20]. Therefore, the operating potential of NaSrLTO increased in samples with a higher Sr content.

Different lithium storage sites in NaLTO and SrLTO result in various amounts of reversibly intercalated Li ions in NaSrLTO. MLTOs host two Li ions per molecular weight at the 4a, 4b and 8c positions of the structure. SrLTO has an additional empty space in the 8f Wyckoff position for Li ions per molecular weight at the 4a, 4b and 8c positions of the structure and electrochemical properties were characterized. The gradual change in the properties.

A drawback to NaSrLTOs may be associated their relatively low specific capacity compared to that of well-known lithium titanium oxide (Li4Ti5O12) [21,22]. Nonetheless, this capacity can be improved due to the extra lithium insertion (red-circled position of the Fig. 3a). Due to the extra position for lithium insertion, samples containing Sr atoms in the crystal structure are able to store more lithium than NaLTO but exhibit 2 different potential plateaus.

A metal of SrLTOs may be associated their relatively low specific capacity compared to that of well-known lithium titanate oxide (Li4Ti5O12) [21,22]. Nonetheless, this capacity can be improved using simple additional processes, such as sol-gel preparation of the precursors or ball-milling as a post-treatment [23]. Additional research and optimization may result in NaSrLTOs becoming competitive anode materials for LIBs because its electrochemical properties can be tuned for the desired applications.

4. Conclusion

NaSrLTOs with various Sr/Na ratios were prepared, and their crystal structures and electrochemical properties were characterized. The gradual change in the operating potential and the amount of reversibly intercalated lithium ions were observed in NaSrLTO from the properties of NaLTO to that of SrLTO as the Sr/Na ratio increased. An analogous crystal structure of MLTO appears to be the reason for the gradual change in the properties.

Conflict of interest

There is no conflict of interest in this work.

Acknowledgments

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