Title
Communication—O3-Type Layered Oxide with a Quaternary Transition Metal Composition for Na-Ion Battery Cathodes: NaTi0.25Fe0.25Co0.25Ni0.25O2

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Rechargeable batteries that reversibly cycle Na ions are a cost-effective alternative to the Li-based technology to meet increasing demand and need for grid-level energy storage. Unlike Li cathode chemistries that heavily rely on Co and Ni, Na-intercalating oxides tend to form energy-dense layered structures with almost all transition metals including Cu, allowing a broad selection and combination of redox centers to tune electrochemical properties and air-stability. In particular, Fe is an attractive metal due to its high redox potential and natural abundance. However, the performance of layered NaFeO₂ as a cathode is impractical; Fe⁺ migration upon desodiation destabilizes the structure, leading to poor Na ion mobility and irreversibility.

The charged state stability of the layered structure, and thereby their electrochemical properties, can be enhanced by partially substituting Fe into redox-inactive elements and/or other transition metals. Li et al. proposed an optimal Fe content that promotes Na diffusion at the high state of charge. Here, we use Ti as a structural stabilizer and report an O₃-type Na transition metal oxide (O₃-NaMO₂) composition, NaTi₀.₂₅Fe₀.₂₅Co₀.₂₅Ni₀.₂₅O₂ (TFCN), for the optimized Fe redox activity. Our results demonstrate a substantial amount of reversible Na intercalation and high rate capability of TFCN, implying that the material may be successfully used as a Na-ion battery cathode.

### Methods

A stoichiometric amount of transition metal precursors (TiO₂, Fe₂O₃, Co₃O₄, and NiCo₂O₄, all from Sigma-Aldrich) was mixed with 20% excess Na₂O (Sigma-Aldrich) by planetary ballmilling at 300 rpm for 4 hours. The resulting mixture was fired at 900 °C for 12 hours under flowing O₂, quenched to room temperature, and transferred to an Ar-filled glove box to prevent air-exposure. The crystal structure and particle morphology of as-prepared TFCN were analyzed by X-ray diffraction (XRD, PANalytical X’Pert Pro) with Rietveld refinement and scanning electron microscopy (SEM, Zeiss, Merlin), respectively. Transition metal oxidation states were probed by X-ray absorption spectroscopy (XAS) obtained at Advanced Photon Source (13ID-E) in Argonne National Laboratory. For half-cell characterization, we used an X-ray absorption spectroscopy (XAS) obtained at Advanced Photon Source (13ID-E) in Argonne National Laboratory. For half-cell characterization, we used an X-ray absorption spectroscopy (XAS) obtained at Advanced Photon Source (13ID-E) in Argonne National Laboratory.

### Results

Figure 1 shows XRD and Rietveld refined profile of TFCN. The material is phase-pure, and all peaks indexed exhibit the R₃m symmetry, corresponding to the O₃ structure. The structure is refined with the hexagonal lattice with a₀ = 2.9768(5) Å and c₀ = 16.012(4) Å, as summarized in Table S1 (Supplemental Material). In accordance with Vegard’s rule, the obtained structural parameters agree with values interpolated from O₃-NaTi₂O₅, O₃-NiCo₂O₄, and O₃-NaFeO₂. The average particle size of TFCN, as determined by SEM, is ~3 μm but we also observe particles up to 10 μm, as shown in the inset. The XAS result suggests that Ti likely remains inert while other transition metals can be redox-active upon cycling.
Figure 2. XAS (K-edge) from (a) Ti, (b) Co, (c) Fe, and (d) Ni of TFCN.

Figure 3a shows voltage profiles of TFCN as a function of specific capacity in a 2–4 V window at C/20. A plateau is present in the voltage profile at \( \sim 2.8 \) V (Na \( \sim 0.75 \)). Charge/discharge capacities at the first, second, and twentieth cycles are 163/145, 147/144, and 130/129 mAh/g, respectively. Compared with results first reported by Yue et al., we obtain improved capacity at this rate, which may result from different electrode preparation methods and/or electrolytes used. An average decay rate of the discharge capacity plotted in Figure 3b is 0.55% per cycle. To investigate how the voltage range affects the overall performance of TFCN, a new charge cutoff is set at 4.2 V. As shown in Figure 3c, it leads to larger discharge capacities: 177/163, 163/160, and 149/146 mAh/g in the first, second, and twentieth charge/discharge, respectively. An additional plateau-like feature at \( \sim 4.1 \) V is found in the first charge but unobservable in the subsequent discharge cycle. The plateau reappears in the second charge and gradually vanishes in further cycles. The average rate of discharge capacity fade is 0.52% per cycle when cycled in 2–4.2 V (Figure 3d).

We further tested the discharge rate capability of TFCN in 2–4.2 V, and Figure 4a shows the voltage–capacity profiles. The cell delivers 163, 158, 153, 141, 123, and 111 mAh/g at C/20, C/10, C/5, 1 C, 5 C, and 10 C, respectively. Remarkably, the capacities achieved at 20 C and 30 C are 95 and 80 mAh/g, respectively, demonstrating high rate performance despite the very large particle size. In Figure 4b, specific energies of TFCN achieved in 2–4.2 V as a function of the C-rate are plotted with those of other O3-Na\( _x \)M\( _{2-2x} \). TFCN indeed exhibits superior electrochemical performance: the specific energies achieved are 504 Wh/kg at C/20 and 200 Wh/kg at 30 C, outperforming many O3-Na\( _x \)M\( _{2-2x} \) compounds.

Discussion

Na content strongly affects the phase stability of O3-Na\( _x \)M\( _{2-2x} \), in which desodiation typically induces phase transition to a P3-type structure that is stable between 0.5 < Na < 0.8. This is a reversible first-order phase transformation that produces a voltage plateau with respect to the capacity, as shown by ex situ XRD in Figure S1 and also commonly observed in O3-Na\( _x \)M\( _{2-2x} \). When desodiated beyond Na \( \sim 0.3 \), the P3-structure may undergo another phase transition that is usually accompanied by an abrupt decrease in c-lattice parameter, leading to either a reversible P3-O3(-O1) phase transformation or irreversible Fe\( ^{4+} \) migration in Fe-containing compositions. In this compound was observed by Yue et al., and other work also showed oxidation of Fe\( ^{3+} \) to Fe\( ^{4+} \) below 4 V. We found the latter in Figure S1. Thus, the reversible and irreversible plateaus at 2.8 and 4.1 V for TFCN in Figure 3c may originate from the O3-P3 transition and Fe\( ^{4+} \) migration, respectively. However, how each transition metal individually contributes to the overall redox reaction and associated structural evolution is unclear at this point.

Na intercalation in Fe-containing Na\( _x \)M\( _{2-2x} \) is very sensitive to the voltage cutoff (i.e., the stability of desodiated structures). For TFCN, the capacity retention is independent of the voltage range in Figure 3. Moreover, the average capacity retention rate and coulombic...
efficiency of TFCN (89% and 98.5% at the 20th cycle, respectively) is higher than that of O3-NaFe0.25Co0.25Ni0.25O2 (84% and 97.3% at the 20th cycle, respectively) even though both materials have the same initial capacity. Thus, Ti may partially stabilize the charged structure, resulting in improved electrochemical properties. Considering that particles of TFCN are micron-sized with random morphology, it is likely that its performance can be improved by further optimization. Moreover, this quaternary system can better tailor the performance of Na-ion batteries by having many different combinations of transition metals. In future work, we will further investigate the effect of Ti substitution on the layered structure and electrochemical properties.

Summary

The electrochemical properties of an O3-type layered sodium quaternary-mixed transition metal oxide, NaTi0.25Fe0.25Co0.25Ni0.25O2, as a positive electrode material for rechargeable Na-ion batteries are demonstrated. The cathode delivers a substantial capacity and exhibits excellent rate capability. Our results show the potential of Ti-doped Na compounds to have high specific energy.

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