Short communication

Electrochemical properties of NaNi$_{1/3}$Fe$_{1/3}$Co$_{1/3}$O$_2$ as a cathode material for Na-ion batteries

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NaNi$_{1/3}$Fe$_{1/3}$Co$_{1/3}$O$_2$ is synthesized by solid-state methods and investigated as a positive electrode material for sodium ion batteries. Galvanostatic cycling of NaNi$_{1/3}$Fe$_{1/3}$Co$_{1/3}$O$_2$ between 2.0 and 4.2 V provides ~165 mAh/g of reversible capacity at C/20. This material also demonstrates great rate-capability and is able to de-intercalate 80 mAh/g even at 30C. First principles calculations are used to determine the order of transition metal oxidation within the system and provide lattice parameters with close proximity to the experimental.

1. Introduction

Na-intercalation batteries are appearing as an important alternative to Li intercalation systems, and rapid progress has been made on developing high capacity cathode materials [1]. It has become clear that the Na analogues of the successful layered LiMO$_2$ electrodes behave very differently from their Li equivalents [2]. The large difference in ionic radius between Li and Na provides a stronger tendency for transition metals to form in the layered structure [3] and from their Li equivalents [2]. The large difference in the Na compounds to form in the layered structure [3–7], and layered Na$_x$M$_{1-x}$O$_2$ (M = Ti, V, Cr, Mn, Fe, Co, Ni) [4–7], as well as several Na compounds with mixed transition metals, Na$_{x}$Ni$_{0.6}$Co$_{0.4}$O$_2$, Na$_{x}$Ni$_{0.5}$Mn$_{0.5}$O$_2$, Na$_{x}$Ti$_{1/3}$Mn$_{1/3}$O$_2$, Na$_{x}$Fe$_{0.5}$Mn$_{0.5}$O$_2$, Na$_{x}$Fe$_{0.5}$Co$_{0.5}$O$_2$, Na$_{x}$Ni$_{0.5}$Mn$_{1/3}$Co$_{1/3}$O$_2$ and Na$_{x}$Ni$_{0.5}$Fe$_{1/3}$Mn$_{1/3}$O$_2$ [18–27], all show electrochemical activity.

In this paper, we report the synthesis and electrochemical performance of NaNi$_{1/3}$Fe$_{1/3}$Co$_{1/3}$O$_2$ as a novel Na intercalation cathode material. The only layered materials in which three transition metals are mixed in the literature are NaNi$_{1/3}$Fe$_{1/3}$Mn$_{1/3}$O$_2$ [26] and Na$_{x}$Ni$_{0.5}$Mn$_{0.5}$Co$_{0.5}$O$_2$ [24], and their capacity is limited to about 120 mAh/g at C/10. We show reversible sodium insertion/extraction with capacities between 165 mAh/g–150 mAh/g when cycled at low rate. Even though the particle size is >1 µm, very high rate capability is achieved, retaining 80 mAh/g discharge capacity at 30C rate. This is promising for high-density high-power Na batteries.

First principles calculations are used to determine the order of transition metal oxidation within the system. In the fully sodiated phase Ni is in a 2+ oxidation state and Fe/Co behaves as a mixed system. As the material is de-sodiated the Fe and Co are first oxidized to 4+ while the Ni goes through two oxidation steps to reach a final oxidation state in the fully de-sodiated structure of Co$^{4+}$, Fe$^{4+}$ and Ni$^{3+}$. 

2. Experimental methods

NaNi$_{1/3}$Co$_{1/3}$Fe$_{1/3}$O$_2$ was synthesized by solid-state reaction. Excess amounts of Na$_2$O, NiO, Co$_3$O$_4$ and Fe$_2$O$_3$ were mixed and ball milled for 4 h at 500 rpm rate, and the resulting material was collected in the glove box. About 0.5 g of powder was fired at 800 °C under O$_2$ for 14 h before it was quenched to room temperature and moved to a glove box filled with argon.

X-ray diffraction (XRD) patterns were collected on a PANalytical X′Pert Pro equipped with Cu Ka radiation in the 2θ range of 5–85°. All the samples were sealed with Kapton film to avoid air exposure. Profile matching of the powder diffraction data of the as-prepared NaNi$_{1/3}$Fe$_{1/3}$Co$_{1/3}$O$_2$ was performed with Highscore Plus using space group R-3m. 

Electrochemical cells were configured with Na/1 M NaPF$_6$ in EC:DEC = 1:1/Na$_{x}$Ni$_{1/3}$Co$_{1/3}$Fe$_{1/3}$O$_2$, Super P carbon black (Timcal, 15 wt.%) as conductive agent, and polyethylene tetrafluoride (PTFE) (DuPont, 5 wt.%) as binder. The 1 M NaPF$_6$ in EC:DEC electrolyte was prepared by dissolving anhydrous NaPF$_6$ (98%, Sigma Aldrich) into EC:DEC (anhydrous, 1:1 in volume ratio). Two pieces of glass fiber served as separators and stainless steel as current collectors in Swagelok cells, assembled in an argon-filled glove box with the moisture level and oxygen level less than 0.1 ppm. The loading density of the active material used was in the range of 2.2–3.1 mg/cm$^2$. The cells were cycled at room temperature using a Solartron 1287 operating in galvanostatic mode and potentiostatic mode.

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3. Computational methods

Energy and charge calculations were performed using the Vienna Ab initio Simulation Package (VASP) [28] within the projector augmented-wave approach [29], using the Perdew–Burke–Ernzerhof (PBE) generalized-gradient approximation (GGA) [30] functional and the GGA + U [31] extension to it. All calculations were performed on a single formula unit cell (NaₓNiCoFeO₆ with x = 0,1,2,3) with sqrt(3) x sqrt(3) ordering for transition metals. This ordering was the lowest energy for the few orderings we considered. Calculations were spin polarized and used a plane wave energy cut-off of 520 eV. The magnetic moments of Co³⁺ and Co⁴⁺ ions were initialized as low spin, which was found to improve convergence in mixed transition metal layered oxide systems.

The U values used for Co, Fe and Ni transition metals are those found by Jain et al. for high-throughput analysis [32] using Wang et al.’s method [33] of fitting the U parameter to experimental binary formation enthalpies for the oxide/fluoride environment. The U values used in these calculations were 3.4 for Co, 4.0 for Fe, and 6.0 for Ni. Charge and voltage analysis was carried out with aid of the pymatgen Python library for materials analysis [34].

4. Results and discussion

The as-prepared NaNi₁/₃Co₁/₃Fe₁/₃O₂ has a O3-layered structure with R-3m symmetry as shown on the XRD pattern in Fig. 1. A SEM image of the as-prepared NaNi₁/₃Co₁/₃Fe₁/₃O₂ is also shown in Fig. 1, with primary particle size >1 μm. The background and three broad peaks between 10° and 30° are due to the Kapton film, which is used to seal the sample. Rietveld refinement gives the lattice parameters a₀hex = 2.951 Å, and c₀hex = 15.854 Å, which are in reasonable agreement to the calculated ones: a₀hex = 2.978 Å, and c₀hex = 15.723 Å. The interatomic distances of (Ni/Fe/Co)–O were calculated from the XRD data to be 2.008 Å (6×) and the transition metals are accommodated at the 3b octahedral sites. The Na–O distance was calculated to be 2.323 Å (6×) and the Na is accommodated at the 3a octahedral sites. Cell parameters and atomic positions are listed in Table 1.

Galvanostatic measurements of charge and discharge of NaNi₁/₃Co₁/₃Fe₁/₃O₂ at C/20 rate (1C = 237 mA/g) at various cycles in the voltage range of 2.0–4.2 V are shown in Fig. 2a. We observe a reversible voltage profile with ≈ 165 mAh/g reversible discharge capacity, and 500 Wh/kg measured energy density which is a significant improvement over previous reports of similar systems with three transition

![Fig. 1](image1)  
**Fig. 1.** XRD pattern (red) and refinement (blue) of as-prepared NaNi₁/₃Co₁/₃Fe₁/₃O₂. The broad peaks between 10° and 30° are due to the Kapton film. The red and blue lines represent the experimental and calculated data respectively. The residual discrepancy is shown in black. The refinement is performed in the R-3m space group and results in R_{wp} = 1.91%, and χ² = 13.76. Particle morphology is observed by SEM analysis.

![Fig. 2](image2)  
**Fig. 2.** (a) Voltage profile of NaNi₁/₃Co₁/₃Fe₁/₃O₂ for multiple cycles at C/20 and cyclic performance at C/20, C/10 and C/5 as an inset. The cells are galvanostatically cycled between 2.0 and 4.2 V; (b) Rate-capability of NaNi₁/₃Co₁/₃Fe₁/₃O₂ in Na cells. The cells were charged to 4.2 V at a rate of C/20 and then discharged at different rates; C/20 (11.86 mA/g)–30C (7116 mA/g). The sample loading of the active material was 2.18 mg/cm²; (c) Comparison between the experimental second voltage profile (red) and calculated composition-averaged voltages (black) of NaNi₁/₃Co₁/₃Fe₁/₃O₂.
metals, such as NaNi$_{1/2}$Fe$_{1/2}$Mn$_{1/2}$O$_2$ [26] and NaNi$_{1/2}$Mn$_{1/2}$Co$_{1/2}$O$_2$ [24] with $\approx 120$ mAh/g, but similar to NaFe$_{1/2}$Co$_{1/2}$O$_2$ [27]. The charge/discharge capacities in the range of 2.0–4.2 V in the first, second, fifth, and tenth cycles are 170/163 mAh/g, 166/163 mAh/g, 157/155 mAh/g, and 153/150 mAh/g respectively. The columbic efficiencies are 96.1% for the first cycle, 97.9% for the second cycle, 98.6% for the fifth cycle and 97.9% for the tenth cycle. We also demonstrate large reversible capacities ($\approx 150$ mAh/g) with small polarization when the material is cycled in the same voltage range (2.0–4.2 V) at rates of C/10 and C/5. The capacity retention at both rates, C/10 and C/5, is 95% and 92% respectively, as one can observe in Fig. 2a. It is important to note that unlike many layered oxides that cannot fully re-insert all sodium, NaNi$_{1/2}$Co$_{1/2}$Fe$_{1/2}$O$_2$ is able to insert up to Na$_{0.99}$ at even cycling to 4.2 V, Fig. 2c.

The ability of the material to discharge to a fully sodiated phase could be contributing to the high reversible capacities that are observed.

Rate capability experiments were run for Na$_x$/NaNi$_{1/2}$Co$_{1/2}$Fe$_{1/2}$O$_2$ cells at rates of C/20 (11.9 mA/g) to 30C (7.12 A/g) as shown in Fig. 2b (1C = 237 mAh/g). The cell continues to deliver large reversible capacities when cycled at faster rates, 1C and 5C, and it’s important to note that the capacities are close to 80 mAh/g even at rates as fast as 30C.

The charge and discharge curves are very similar over twenty cycles, indicating a reversible transformation path upon charge and discharge. Similar behavior with large steps in the voltage curve has also been observed for de-intercalation of Na from NaNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$, NaNi$_{1/3}$Mn$_{1/3}$Fe$_{1/3}$O$_2$, and NaFe$_{1/2}$Co$_{1/2}$O$_2$ [22,24,27].

First principles calculations were performed at compositions NaNi$_{1/3}$Fe$_{1/3}$Co$_{1/3}$O$_2$, Na$_2$Ni$_{1/3}$Fe$_{1/3}$Co$_{1/3}$O$_2$, NaNi$_{1/3}$Fe$_{1/3}$Co$_{1/3}$O$_2$, and NaNi$_{1/3}$Fe$_{1/3}$Co$_{1/3}$O$_2$ in order to estimate the average voltages between these compositions and to determine the order of transition metal oxidation. We find that in the fully sodiated material Ni is close to a $+2$ oxidation state and the Co and Fe states are mixed in a state that is partially oxidized to $+3.5$. Upon de-sodiation, the Fe/Co system is first oxidized to Fe$^{4+}$ and Co$^{4+}$ at 2.72 V followed by Ni$^{2+}$ oxidation to 3+ and 4+. The horizontal lines in Fig. 2c represent the calculated average voltage in each composition domain [35], and should not be interpreted as an actual voltage curve. While the resulting average voltages are in good agreement with the experimental averages, the somewhat uncommon oxidation state needs experimental confirmation.

NaFeO$_2$ was recently revisited and shows a reversible capacity of 80 mAh/g at the limited cutoff of 3.4 V [36]. It is observed that at higher voltages NaFeO$_2$ goes through an irreversible structure transition, which is presumably associated with partial migration of iron [36]. Materials such as NaNi$_{1/3}$Fe$_{1/3}$Co$_{1/3}$O$_2$, NaNi$_{1/3}$Fe$_{1/3}$Mn$_{1/3}$O$_2$, NaFe$_{1/2}$Co$_{1/2}$O$_2$, and NaFe$_{1/2}$Mn$_{1/2}$O$_2$ further demonstrate that the substitution of Fe in NaFeO$_2$ with different elements such as nickel/cobalt, nickel/manganese, cobalt and manganese respectively can be very effective in suppressing iron migration in NaFeO$_2$ and provide high reversible capacities and great rate capabilities.

Designing innovative cathode materials based on abundant elements such as sodium and iron is very important. As Yoshida et al. pointed out cobalt is not an abundant element and its utilization should be reduced [27]. With a careful approach our study demonstrates that the nickel substitution is reducing the amount of cobalt without altering the reversible capacities and rate capabilities that these O3-type combinations provide.

5. Conclusions

In this article, we have studied O3-type NaNi$_{1/2}$Co$_{1/2}$Fe$_{1/2}$O$_2$ system as a positive electrode material for rechargeable sodium batteries. This material delivers $\approx 165$ mAh/g of reversible capacity with an energy density of $\approx 500$ Wh/kg at C/20. NaNi$_{1/3}$Fe$_{1/3}$Co$_{1/3}$O$_2$ shows excellent rate-capability with 80 mAh/g at 30C and with 92% capacity retention even at C/5 rate. The electrochemical properties and the voltage profile are very similar to NaFe$_{1/2}$Co$_{1/2}$O$_2$, which signifies the importance of Ni substitution on maintaining the excellent rate capability and reversibility of the Fe-Co based materials while reducing the consumption of Co.

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