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Authors

Doeff, Marca
Shirpour, Mona
Cabana, Jordi

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New materials based on a layered sodium titanate for dual electrochemical Na and Li intercalation systems

Marca Doeff, Mona Shirpour, and Jordi Cabana

Environmental Energy Technologies Division
Lawrence Berkeley National Laboratory
Berkeley, CA 94720

In many ternary alkali titanates, TiO_6 octahedra share corners and/or edges to form two-dimensional structures. The titanate layers are negatively charged, and positively charged species such as alkali metal cations (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+) or protons (H^+) are located between the galleries. The nature of these intercalated cations, the synthesis conditions, structure, and surface properties of the octahedral layers tune the interlayer distance and properties of the layered titanate. The versatility of the structural properties makes these materials ideal for a number of applications including ion-exchange, nuclear waste clean-up, and photocatalysis.

In this work, we report a new layered titanate phase, derived from the $\text{NaTi}_3\text{O}_6(\text{OH})\cdot 2\text{H}_2\text{O}$ structure, that is capable of reversibly intercalating both Li and Na at very low potentials. The structure of $\text{NaTi}_3\text{O}_6(\text{OH})\cdot 2\text{H}_2\text{O}$ (NNT) consists of edge- and corner-sharing TiO_6 octahedra that form corrugated layers of $\{\text{Ti}_6\text{O}_{14}\}^+$ units, between which hydrated Na^+ cations and protons (H^+) are located (Figure 1) [1]. Capacities as high as 300 mAh/g are predicted for the dehydrated version of $\text{NaTi}_3\text{O}_6(\text{OH})\cdot 2\text{H}_2\text{O}$, based on reduction of all of the Ti^{4+} ions to Ti^{3+} . We describe the structural changes during dehydration and report results obtained with both as-made and dehydrated materials in lithium and sodium half-cell configurations for the first time.

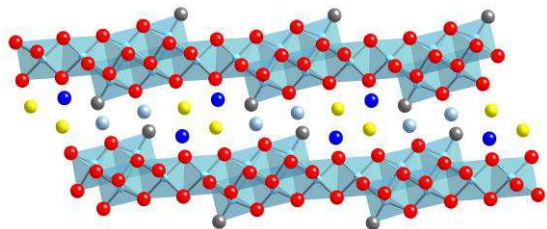


Figure 1. Crystal structure of $\text{NaTi}_3\text{O}_6(\text{OH})\cdot 2\text{H}_2\text{O}$ created with CrystalMaker software. TiO_6 octahedra are in blue, yellow spheres are Na^+ ions, red spheres are O^{2-} ions dark and light blue spheres are H_2O groups coordinated to Na^+ , and grey spheres are OH^- groups connected to Ti^{4+} .

Figures 2 present the first and second cycle voltage profiles of composite electrodes containing the as-made or the dehydrated NNT in Na and Li half-cells. It was found that this material can reversibly intercalate both lithium and sodium. The initial specific discharge capacities, as measured in half-cells, varied with the state of hydration and the nature of the counter-electrode (Na or Li). The electrochemical potential showed a non-linear sloping dependence with degree of intercalation, indicative of a solid-solution mechanism of intercalation. The process was centered at a low average potential of about 0.3V vs. Na or Li, the lowest ever reported for titanate-based Li hosts. The dehydrated compound showed better cycling reversibility than the as-made material.

The high theoretical capacity, low insertion potentials, and solid solution intercalation mechanism of the dehydrated material have important implications for the development of high energy density dual intercalation systems based on either sodium or lithium.

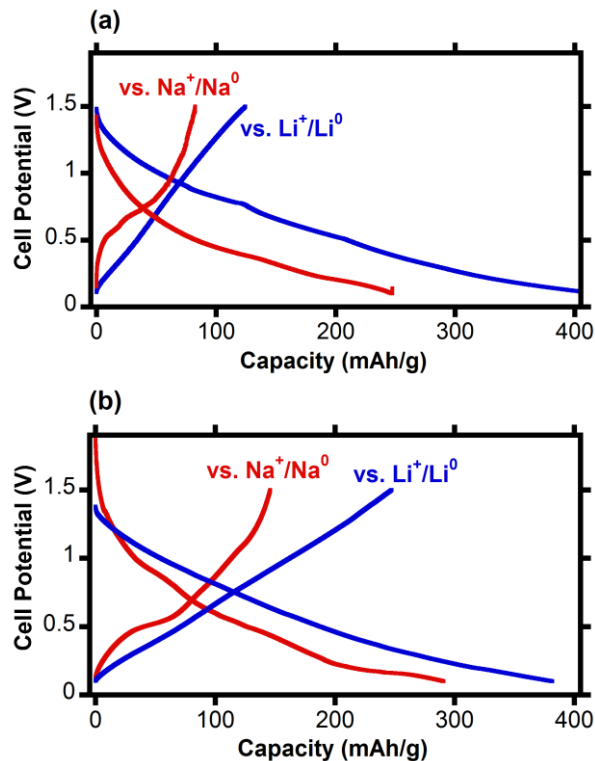


Figure 2. Voltage versus specific capacity profile for (a) the as-made NNT, and (b) the dehydrated NNT in Na and Li half-cells cycled between 1.5 and 0.1 V at 0.15 mA/cm² (30 mA/g).

References

- [1] I. Andrusenko, E. Mugnaioli, T. E. Gorelik, D. Koll, M. Panthofer, W. Tremel and U. Kolb, *Acta Crystallographica Section B-Structural Science*, 2011, 67, 218-225.

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