

Comparative Electrochemistry of Sodium and Lithium Intercalation in Mixed-Alkali Transition Metal Oxide Cathodes: Insight into Structure and Reactivity

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Introduction

Sodium-ion electrochemical energy storage is rapidly developing as a complementary technology to well established Li-ion systems. We have been exploring the layered oxide materials space AMO_2 ($A = \text{Li, Na; M} = \text{Mn, Ni}$), incorporating both sodium and lithium in the alkali metal complement, as cathodes for sodium-ion systems. Alkali transition metal oxides typically crystallize in similar layered structures where the 2D nature of the compound readily accommodates alkali ions of different size by simply expanding the distance between transition metal slabs. Their well-developed intercalation chemistry and high energy densities have made them the premier class of cathode materials in ambient temperature, non-aqueous lithium-ion and sodium-ion batteries.

Experimental Results

The compositional range $\text{Na}_{1.2-x}\text{Li}_x\text{Ni}_{0.25}\text{Mn}_{0.75}\text{O}_{2+\delta}$ ($0 < x < 0.6$, $\delta \approx 0.35$) was investigated by high resolution x-ray powder diffraction and ^6Li NMR. The predominant structure is that of the hexagonal $\text{Na}_{0.7}\text{MnO}_2$ archetype (space group $P6_3/mmc$), although there is a set of weak peaks corresponding to the monoclinic Li_2MnO_3 phase (space group $C2/m$, marked by \blacklozenge in **Figure 1**) that grows in intensity as the lithium content increases. ^6Li MAS NMR confirms that lithium resides in several different environments in these compounds including the lithium metal layers and transition metal layers of Li_2MnO_3 -like domains (*i.e.*, with six Mn nearest neighbors in the transition metal slab) and also in the transition metal slabs of a layered sodium phase, in this case also in the vicinity of Ni atoms.

These compounds are viewed as “layered-layered” composite cathode materials in which one of the layered components has an expanded interlayer spacing along the c -axis to accommodate the sodium atoms. They exhibit good performance as cathodes in sodium-ion systems,¹ but can also be directly cycled in lithium-ion systems, via an *in situ* electrochemical ion exchange. The galvanostatic cycling profiles shown in **Figure 2** demonstrate that, compared to sodium, more lithium ions can be inserted into the structure per formula unit, presumably by accessing a structural component that is unavailable to the larger sodium ions. The nature of this effect across the series of compounds with varying alkali metal ratios will be presented and discussed in the context of the mechanism of reactivity and implications for the synthesis of new sodium-ion intercalation compounds.

Reference

- Slater, M. D.; Kim, D.; Lee, E.; Johnson, C. S.; *Advanced Functional Materials*, **23**, 947 (2013).

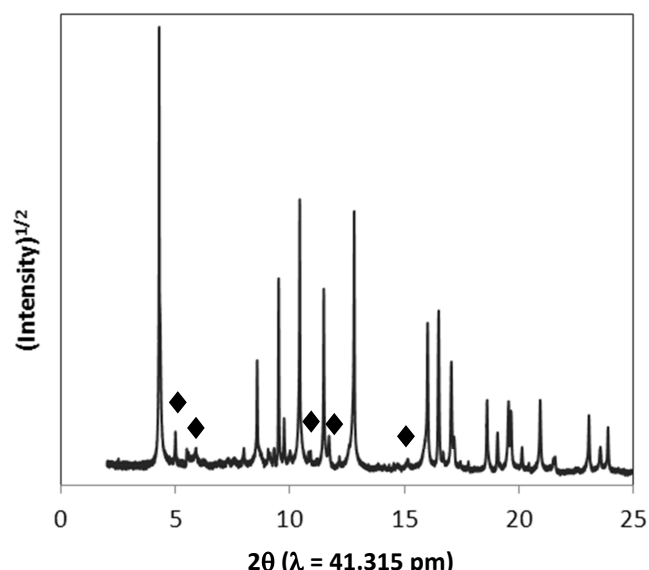


Figure 1. HRXRD of $\text{Na}_1\text{Li}_{0.2}\text{Ni}_{0.25}\text{Mn}_{0.75}\text{O}_{2.35}$ was performed at Sector 11BM of the Advanced Photon Source; presented with the vertical axis as the square root of intensity to emphasize weak peaks.

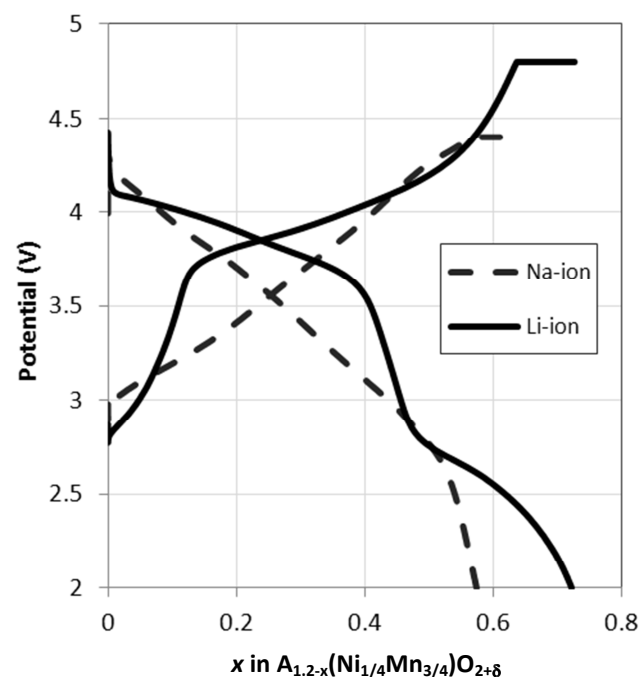


Figure 2. Voltage profile of the 5th cycle of $\text{Na}_1\text{Li}_{0.2}\text{Ni}_{0.25}\text{Mn}_{0.75}\text{O}_{2.35}$ evaluated in Na-ion and Li-ion configurations: alkali metal foils with respective electrolytes APF₆ in carbonate ester solvents; laminate electrodes (approximate active material loading of 4 mg/cm²) were cycled at 15 mA/g.

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