

Nuclear Magnetic Resonance Studies of Sodium Titanate Cathode Materials for Na-ion Batteries.

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The electrochemical properties of materials derived from $\text{NaTi}_3\text{O}_6(\text{OH})\cdot 2\text{H}_2\text{O}$ have been investigated recently.¹ The parent compound has a corrugated layered structure consisting of $\{\text{Ti}_6\text{O}_{14}\}^{4-}$ units with hydrated sodium cations and protons in the interlayer spaces. Upon heating to 600°C, water is removed irreversibly, the interlayer distances become smaller, and connecting bonds between the octahedral layers form. It was found that this material can reversibly intercalate both lithium and sodium.¹

In order to characterize the Na^+ ionic environment as a function of sample treatment conditions including dehydration at elevated temperature and electrochemical cycling, we have undertaken a series of ^{23}Na nuclear magnetic resonance (NMR) measurements on these materials. Both high resolution magic angle spinning (MAS) as well as static NMR spectra were collected, the reason for the latter being to observe detailed nuclear quadrupole splittings and lineshapes which are very sensitive to small local structural variations.

Figure 1 displays the ^{23}Na MAS (with 35kHz spinning speed) NMR spectra of the as-synthesized $\text{NaTi}_3\text{O}_6(\text{OH})\cdot 2\text{H}_2\text{O}$ compound and a sample subjected to heat treatment to drive out the structural water molecules.

Figure 2 shows the corresponding static NMR spectra. Clear differences are observed in both sets of spectra indicating significant changes in local ionic environments. In particular, the dehydrated material exhibits much broader linewidths under both low and high resolution conditions, which is attributed to a combination of higher local symmetry and ionic mobility in the as-prepared materials.

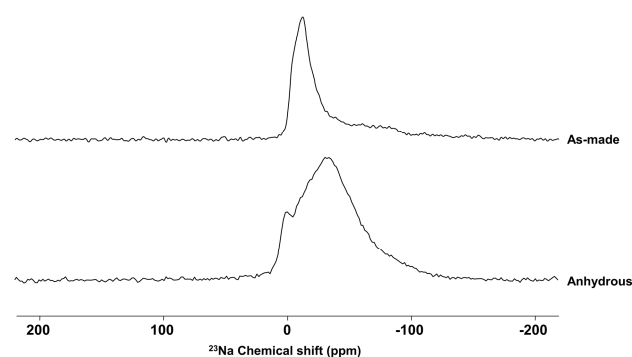


Fig. 1. ^{23}Na MAS spectra of as-prepared (top) and dehydrated (bottom) $\text{NaTi}_3\text{O}_6(\text{OH})\cdot 2\text{H}_2\text{O}$.

We have also obtained MAS and static ^{23}Na NMR spectra for these cathode materials harvested from coin cells, in which the samples were electrochemically cycled and these results will be presented, with emphasis on correlating local structure with electrochemical performance. Finally, because these materials are also electrochemically active towards Li, we have also conducted ^7Li NMR measurements on lithiated samples as a function of state of charge and cycling.

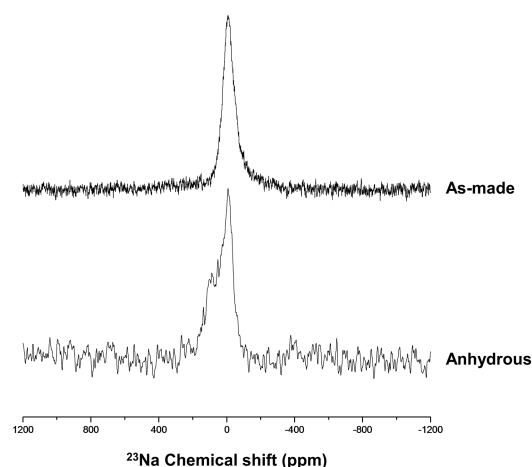


Fig. 2. ^{23}Na static spectra of as-prepared (top) and dehydrated (bottom) $\text{NaTi}_3\text{O}_6(\text{OH})\cdot 2\text{H}_2\text{O}$.

References:

1. Mona Shirpour, Jordi Cabana, and Marca Doeff, *Energy & Environ. Sci.*, in press

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