Transport properties of ordered and disordered spinel $LiMn_{1.5}Ni_{0.5}O_4$

Ruhul Amin, Alan Ransil, Dorthe B. Ravnsbaek and Yet-Ming Chiang

Massachusetts Institute of Technology (MIT)
Department of Materials Science and Engineering
77 Massachusetts Avenue, Cambridge, MA 02139

Abstract

$LiMn_{1.5}Ni_{0.5}O_{4-\delta}$ (δ = 0-0.05) (LMNO) is a high voltage cathode material for lithium ion batteries that has attracted much attention within the battery community due to its high power and greater energy density than purely manganese spinel. LMNO exhibits ordered and disordered polymorphs in which the arrangement of Mn and Ni differ in the spinel structure[1]. The degree of disorder varies with heat treatment conditions, and influences the transport properties and related electrochemical performance. Although differences in charge-discharge behavior of the two structures have been reported by several research groups, the mechanistic origin is not clearly understood. Many of the unknown questions can be resolved if the transport properties of the material are reliably characterized. To date only the electronic conductivity of the fully lithiated phase of LMNO has been measured[2]. Here we report measurements of the ionic and electronic conductivities as well as ionic diffusivity of the ordered and disordered phases, measured separately using ion and electron blocking cell configurations. The measurements have been performed by direct current polarization technique and impedance spectroscopy on additive-free sintered samples. Furthermore, these transport properties have been measured as a function of lithium content as well as of temperature.

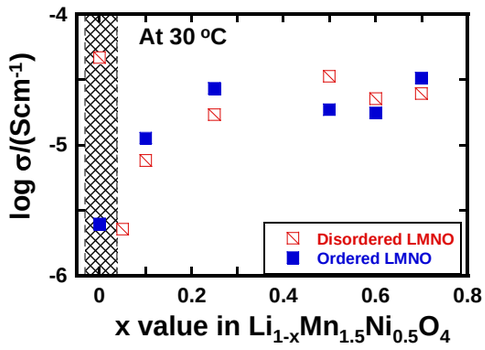

Fig. 1 Electronic conductivities of ordered and disordered LMNO as a function of lithium content at 30°C.

We found that the electronic conductivity of the ordered phase increases with lithium removal (electrochemically) up to about 25% delithiation, after which the conductivity remains almost constant with further delithiation (cf. Fig. 1). In contrast, the disordered phase exhibits a sudden drop of conductivity upon initial delithiation at the 4.1 volt plateau, which is associated with conversion of Mn^{3+} to Mn^{4+}. Thereafter, it exhibits similar conductivity behavior to the ordered structure. The ionic conductivities and diffusivities of the ordered and disordered fully lithiated phases are of similar magnitude, as shown in Table I. Initial measurements of partially delithiated phases indicate decreasing ionic conductivities and diffusivities upon delithiation.

Thus no major differences are observed in the transport properties of ordered and disordered LMNO, except for higher electronic conductivity of disordered LMNO in the fully lithiated state. From these data, it is clearly seen that electronic conductivity is not rate limiting in either phase, and that the lithium ion diffusivity is high enough to permit electrochemical cycling of micron-scale particles at relatively high C-rates (i.e., up to about 10 μm diameter or a 2.5C-rate). However, it is noted that the present measurements are carried out with minimal perturbation to the Li content of the sample, namely in the absence of electrochemical titration, and that the rate limiting mechanism(s) accompanying large electrochemical excursions may differ.

Table I Comparison of ionic conductivity and diffusivity of ordered and disordered LMNO at 50°C

Spinel Phases LMNO	Ionic conductivity (Scm-1)	Diffusivity (cm^2s^{-1})
Ordered	~5.00×10^{-8}	~1.50×10^{-7}
Disordered	~4.00×10^{-8}	~5.50×10^{-8}

References

1. J. Cabana, M. Casa-Cabanas, F. O. Omenya, N. A.D. Zeng, Chernova, M. S. Whittingham and C. P. grey, Chem. Mater, **24**, 2952 (2012).
2. M. Kunduraci, J. F. Al-Sharab and G. G. Amatucci, Chem. Mater., **18**, 3585 (2006)