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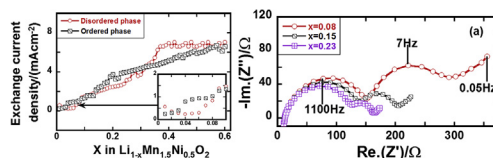
Part-II: Exchange current density and ionic diffusivity studies on the ordered and disordered spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode

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HIGHLIGHTS

- Measurement of exchange current density at the interface of $\text{Li}_{1-x}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$.
- Determination of lithium ion diffusivity as a function of lithium content and temperature.
- Li^+ -ion diffusivity is the limiting factor in higher states of charge of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.
- Charge transfer kinetics is the limiting factor in lower states of charge of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

GRAPHICAL ABSTRACT



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ABSTRACT

Additive-free pellets of $\text{Li}_{1-x}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ have been prepared for the purpose of performing ionic diffusivity and exchange current density studies. Here we report on the characterization of interfacial charge transfer kinetics and ionic diffusivity of ordered ($P4_332$) and disordered ($Fd\bar{3}m$) $\text{Li}_{1-x}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ as a function of lithium content at ambient temperature. The exchange current density at the electrode/electrolyte interface is found to be continuously increased with increasing the degree of delithiation for ordered phase (~ 0.21 – 6.5 mA/cm^2) at ($x = 0.01$ – 0.60), in contrast the disordered phase exhibits gradually decrease of exchange current density in the initial delithiation at the 4 V plateau regime ($x = 0.01$ – 0.04) and again monotonously increases (0.65 – 6.8 mA/cm^2) with further delithiation at ($x = 0.04$ – 0.60). The ionic diffusivity of ordered and disordered phase is found to be $\sim 5 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ and $\sim 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, respectively, and does not vary much with the degree of delithiation. From the obtained results it appears that the chemical diffusivity during electrochemical use is limited by lithium transport, but is fast enough over the entire state-of-charge range to allow charge/discharge of micron-scale particles at practical C-rates.

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1. Introduction

Electrochemical devices, including fuel cells and batteries, are playing an increasing role in our live, particularly as societies shift toward renewable energies and low-carbon economy. In order to satisfy the rising demand for affordable and reliable lithium-ion batteries for mobile and stationary energy storage applications, the development of high energy density active materials becomes a

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priority. Amongst cathode candidates, the spinel material $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is especially attractive owing to its high operating cell voltage (4.7 vs Li/Li^+) [1–6]. However, in order to accelerate its introduction across a range of applications, an improved understanding of the material's bulk and interfacial properties is required. Indeed, the impact of the interfacial kinetics on the performance of electrochemical devices has been widely demonstrated, particularly by investigating the exchange current which is crucial for optimizing and modeling battery performances [7–9]. While particle size reduction, which is in general accompanied by an increase of surface area, reduces the current density necessary to charge or discharge the particle at a given C-rate and lowers the interfacial over-potential required to drive the electrochemical charge-transfer reaction, there is, however, a possibility of intensifying parasitic reactions, particularly in the case of the high voltage spinel.

It is worth mentioning that atomic-level migration of transition metals ions had been observed during the cycling of the spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode [10], leading to the dissolution of Ni- and Mn-ions and building-up of the charge transfer impedance, which significantly contributes to the rapid deterioration of the battery performances [10]. Therefore, it is essential to get a deeper understanding of the interfacial properties of the spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. The charge-discharge behavior of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, having both the ordered and disordered spinel structures, had been investigated by several research groups [2–6]. However, there are discrepancies with regard to the suitability of the disordered or ordered spinel for better battery performance [4–6]. It is also not clearly understood whether the rate performance of the material is limited by bulk transport properties or interfacial charge transfer reaction kinetics.

A few studies reported Butler-Volmer's exchange current density values for some anode [11–15] and cathode [16–20] materials, wherein the current density is given by the following equation [21]:

$$J = J_0 \left(e^{\frac{\alpha F}{RT} \eta} - e^{-\frac{(1-\alpha)F}{RT} \eta} \right) \quad (1)$$

J is the current density; J_0 is the exchange current density which is an intrinsic property of materials that encompasses structure and composition effects at the solid/electrolyte interface; α is the transfer coefficient (typically 0.5); F is the Faraday's constant (96485 J mol^{-1}); R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$); T is temperature; and η is the over-potential. Exchange current density data of some anodes and cathodes are summarized in Table 1. The measurements had been performed on composite electrodes by electrochemical impedance spectroscopy (EIS) [17,20], galvanostatic intermittent titration (GITT) [18], cyclic voltammetry (CV) and potentiostatic intermittent titration technique (PITT) [11,13]. The variability in the reported exchange current data likely originates from the poorly defined electrode-electrolyte interfacial area due to the composite nature of the studied electrodes. Indeed, several parameters, such as the amount of inactive materials (carbon additive and binder) and degree of mixing during

the preparation of composite electrodes, can influence the consistency of measurements and thus make it difficult to extract reliable intrinsic exchange current density of electrochemically active materials.

The purpose of the present work is to elucidate the role of the electrochemical charge transfer kinetics at the electrode/electrolyte interface of $\text{Li}_{1-x}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ in determining the rate performance of the spinel cathode. Of significance, a study detailing the results of measurements of exchange current density and ion diffusivity is reported on additive-free sintered $\text{Li}_{1-x}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ pellets having the ordered and disordered spinel structure in order to exclude any extrinsic effect.

2. Experimental

2.1. Preparation of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ pellets

Spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powder was acquired from NEI Corporation. The phase purity of the supplied powder was checked by x-ray diffraction. Compacted pellets were prepared by pressing the powder at 340 MPa for 60s, forming cylindrical samples of 14 mm in diameter. The pellets were sintered using two heat treatment procedures to obtain the ordered and disordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. In the case of the disordered spinel (labeled D-LNMO), the pellets were heated in air at 1000 °C for 24 h and subsequently annealed at 725 °C for 12 h with heating and cooling rates of 10 °C/min (procedure 1); whereas in the case of the ordered spinel (labeled O-LNMO), the pellets were calcined at 1000 °C for 24 h followed by annealing at 650 °C for 48 h and cooling at 1 °C/min, all under argon:oxygen (1:1) atmosphere (procedure 2). The relative density was measured using analytical balance (KERN ABT-A01) according to Archimedes principle. The prepared pellets had relative densities in the range of 80–85%. Higher temperatures sintering was tried to achieve higher densities, however, the final pellets contained rock-salt impurity phases.

The sintered pellets were characterized by x-ray diffraction, Raman spectroscopy and electrochemical charge to distinguish between $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ in the ordered and disordered forms. Details on characterization and analysis are provided in part 1 of this work [22]. Scanning electron microscopy (SEM) analysis was performed on the sintered polished pellets using the machine (FEI/Philips XL30ESEM).

2.2. Electrochemical delithiation

The sintered pellets of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ were polished to thicknesses between 0.20 mm and 0.24 mm. One side of the polished pellets was coated with a thin layer of carbon to ensure good electrical contact with the metal current collectors in the cells. The delithiation process was performed in a Swagelok-type electrochemical cell using lithium metal foil as the counter electrode, the pellet of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ as the working electrode, and a liquid electrolyte comprised of 1 M LiPF_6 dissolved in ethylene carbonate/

Table 1
Comparison of exchange current density values for several electrode materials.

Materials	Exchange Current Density (mA/cm^2)	Electrolyte used	References
$\text{Li}_{1-x}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$	0.23–6.8	1 M LiPF_6 in EC/DEC	This work
Silicon	10^{-10} –1	M LiPF_6 in EC/DMC	[10,12]
Graphite	1–2.3	M LiPF_6 in EC/DMC	[13]
$\text{Li}_4\text{Ti}_5\text{O}_{12}$	0.81	1 M LiPF_6 in EC/DEC	[14]
LiCoO_2	0.025–0.1, 2.5–6.2	1 M LiPF_6 in EC/EMC/DMC	[15,16]
LiFePO_4	0.17	1 M LiPF_6 in EC/DEC	[17]
$\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$	0.25–23.6	1 M LiPF_6 in EC/EMC/DMC	[18]

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