



Separating electronic and ionic conductivity in mix-conducting layered lithium transition-metal oxides

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HIGHLIGHTS

- A method is developed to resolve electronic and ionic conductivities of cathodes.
- Large electronic and ionic conductivities are observed for the Ni-rich NMCs.
- Variations in the two conductivities by introducing Ni are well interpreted.

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ABSTRACT

Electronic and ionic conductivities of active materials are the fundamental properties in determining the dynamical behavior and rate performance of batteries, yet, they are typically hard to be distinguished due to the convolution of the two conduction processes, the complexity of the dynamic responses in composite electrodes, and other extrinsic factors such as porosity and interfacial effects. Herein, we report a simple and reliable method that combines the electrochemical impedance spectroscopy with direct-current polarization to accurately resolve the electronic and ionic conductivities of conventional layered cathode materials for Li-ion batteries, including LiCoO_2 and $\text{LiNi}_{1-x-y}\text{Mn}_x\text{Co}_y\text{O}_2$. A significant increase in the electronic conductivity was observed with the increasing Ni content, accompanied by a large decrease in the activation energy. Meanwhile, a similar variation trend in Li^+ conductivity was observed, together with a large decrease in the Li^+ hopping barrier. These can be attributed to the variations in electronic structure and defect chemistry, the apparent lattice expansion with incorporating Ni, especially along the *c*-axis, as well as a weakened Li^+ -transition metal interaction via decreasing the Mn^{4+} content.

1. Introduction

Li-ion batteries (LIBs) are one of the most important energy storage devices for the future energy and environmental landscape of the world. Currently, LIBs have been widely used in portable electronics and a growing number of electric vehicles in hope to fully replace the conventional internal combustion vehicles. The strong market incentive and environmental concerns significantly drive the battery manufacturers to produce cost effective, high energy, and high power batteries. Among various cathodes for the high energy LIBs, Ni-rich $\text{LiNi}_{1-x-y}\text{Mn}_x\text{Co}_y\text{O}_2$ (NMCs, $1-x-y \geq 0.5$) are one of the most promising candidates due to their relatively high energy density, low cost (compared to LiCoO_2), and high power capability [1,2]. To widely commercialize these promising materials, their fundamental properties, including electrochemical and physical properties, need to be fully understood. Unlike the consensus reached in their well-studied thermodynamic

properties, e.g., specific capacity and energy density, the kinetic behavior of NMCs, such as power capability, is still poorly understood and some contradictory results have been reported [3–7] in the past.

Power capability of a LIB is primarily determined by the electronic transport and Li^+ diffusion processes in the electrodes [8]. A basic knowledge of the intrinsic electronic (σ_e) and Li^+ (σ_i) conductivities of the electrode materials is crucial for understanding the electronic and Li^+ transport processes and rate capability in the composite electrodes (normally contain active materials, conductive carbon, and binder) and for designing high-performance LIBs, because the charge and ion transport within the active particles and/or across their interfaces are the rate-limiting processes. Yet some fundamental transport properties have been poorly interpreted, even for the commercial LiCoO_2 [3]. σ_e of LiCoO_2 has been determined to be 10^{-10} – $10^{-2} \text{ S cm}^{-1}$ under various conditions, depending on the testing techniques, sample geometry, doping level, degree of lithiation, etc. [3,9,10]. Similarly large

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variations in Li^+ diffusivity (D_{Li^+} : 10^{-14} – 10^{-8} $\text{cm}^2 \text{s}^{-1}$) can be found in the literature [11–14], while σ_i (can be expressed using the Nernst–Einstein equation as $\sigma_i = n_i e^2 D_{\text{Li}^+} / k_b T$, where n_i is the Li^+ concentration and e the elementary charge, k_b the Boltzmann constant, and T the absolute temperature) is much less characterized due to the difficulty in separating the two convoluted conduction processes [15]. Typically, σ_e and D_{Li^+} are determined in different samples using different techniques; for instance, sintered pellets or thin films were used to obtain σ_e using the four-probe method [10,16,17], polarization [15], or electrochemical impedance spectroscopy (EIS) [11,13], while the composite electrodes with conductive carbon and binder in liquid cells were utilized to derive the chemical diffusion coefficient $D_{\text{Li}^+}^C$ by cyclic voltammetry (CV) [18], galvanostatic intermittent titration technique (GITT) [19,20], or EIS [3,10,21,22]. This brings about additional complexities and uncertainties in discerning the intrinsic electronic and ionic transport properties of the active materials. In particular, $D_{\text{Li}^+}^C$ derived indirectly from the dynamic response of an entire electrochemical cell is normally quite different from the self-diffusivity D_{Li^+} and highly unreliable because of the non-uniform potential distributions, complex geometry, and the competing kinetic processes, etc. The situation gets even more complicated for the NMCs, especially the nickel-rich NMCs, due to the different levels of cation mixing, complex phase transitions, and sample surface contamination. Hence, a simple and reliable technique is needed to accurately determine the intrinsic σ_i and σ_e of the electrode materials.

In this study, a method combining the EIS with direct-current (DC) polarization was developed to separately measure σ_i and σ_e of LiCoO_2 and NMCs. σ_i and σ_e were determined in the same polycrystalline pellets directly sintered from the electrode active material powders by the spark plasma sintering (SPS) technique. SPS can efficiently and quickly compact the electrode powders at relatively low temperatures (~ 800 °C in 5 min), and meanwhile, activate the particle surfaces and clean the grain boundaries by electrical field induced plasma, providing ‘clean’ and simple specimens to study intrinsic σ_i and σ_e . σ_e values determined by the EIS and DC polarization show excellent agreement, cross-validating our technique. With the increasing Ni content, both σ_i and σ_e increase significantly, accompanied by considerable reductions of the activation barriers for both electrons and ions. The increase in σ_i and σ_e well accounts for the significantly improved rate capability of the nickel-rich NMCs and can be interpreted by the modifications of electronic band structure, lattice parameter, and Li^+ - cation interactions, etc.

2. Experimental section

2.1. Materials and characterization

LiCoO_2 , $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (NMC333), and $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ (NMC532) powders were purchased from MTI Corporation (USA), and $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ (NMC622) and $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (NMC811) powders were obtained from the Battery500 Consortium (funded by the US Department of Energy’s Office of Energy Efficiency and Renewable Energy). All materials were stored in a glovebox and used as received, and special attention was paid to handling high-Ni NMCs (NMC532, NMC622, and NMC811) to reduce air and moisture exposure, especially NMC811. The received powders were sintered into dense pellets with a diameter of ~ 12.5 mm and a thickness of ~ 2 – 3 mm by the SPS technique at 800 °C under a uniaxial pressure of 40 MPa for 5 min. The relative densities of the sintered pellets are higher than 98%.

Phase purity and crystal structure were investigated by the powder X-ray diffraction (XRD, Bruker D8 Advance, Germany). XRD refinements were performed using the DIFFRAC TOPAS V5 software (Bruker, Germany). Morphologies of the original powders and fractal surfaces of sintered samples were examined using either a field-emission scanning electron microscope (Sirion XL30, FEI, USA) or a Phenom ProX SEM (Phenom-World, The Netherlands).

2.2. Electrochemical test

Coin-type cells (half-cell with Li metal anode) were used to test the electrochemical properties of the cathode materials. The electrodes were prepared by thoroughly mixing 80 wt% active materials, 10 wt% carbon black (TIMCAL Graphite & Carbon super P, MTI Corporation, USA), and 10 wt% polyvinylidene fluoride (PVDF, MTI Corporation, USA) in N-Methyl-2-pyrrolidone (NMP, Sigma Aldrich, USA). The slurries made by a planetary centrifugal mixer (30 min, ARE-310, Thinky, USA) were cast on Al foils by an automatic film coater with a doctor blade (MSK-AFA-II-VC-FH, MTI Corporation, USA). Al foils with coatings were then dried in vacuum at 120 °C for 12 h to get rid of the NMP solvent. The typical active material loading is ~ 7 mg cm^{-2} . All electrodes were stored in an Ar-filled glove-box before use (Lab Star, Mbraun, Germany, $\text{H}_2\text{O} < 0.5$ ppm, $\text{O}_2 < 0.5$ ppm). The electrodes were punched into discs with a diameter of 12.7 mm. The cathodes were assembled in 2032-type coin cells with 250 μm thick Li foils (MTI Corporation, USA) as the anodes, 25 μm polypropylene membranes (Celgard 2500, USA) as the separators, and a solution of 1.0 mol L^{-1} LiPF_6 in ethylene carbonate and ethyl-methyl carbonate (3:7 wt./wt.) with 2 wt% vinyl-carbonate as the electrolytes. Cyclic voltammograms (CVs) were collected between 2.8 and 4.4 V (vs. Li^+/Li) at 20 °C using a VersaSTAT 4 potentiostat (Ametek Scientific Instruments, USA), under scanning rates ranging from 0.1 to 1.0 mV s^{-1} . The coin cells were cycled galvanostatically between 2.8 and 4.4 V (vs. Li^+/Li) at 25 °C using LANDT battery testers (Landt Instruments, China).

2.3. EIS and DC polarization

EIS and DC polarization were performed on the dense pellets of LiCoO_2 and NMCs using a PARSTAT 4000A Potentiostat (Ametek Scientific Instruments, USA) in the temperature range from -20 to 100 °C in a temperature chamber (Maccor, USA), and the samples were well sealed under vacuum during the test to avoid air and moisture contaminations. EIS tests were carried out in the frequency range from 0.01 Hz to 10 MHz with an AC amplitude of 50 mV. DC polarizations were conducted in the voltage range from -2 to 2 V (-3 – 3 V for LiCoO_2 due to its large resistance). Prior to EIS and DC polarization measurements, Ag paste was sprayed on both sides of pellets and heated in vacuum at 110 °C for 2 h to vaporize the solvent. The geometry of the testing sample is schematically shown in Fig. 1(a), where the Ag electrodes are electron-conducting but ion-blocking. The EIS method determining the ionic and electronic conductivities in this study follows the Huggins’s method [23], in which the two semicircles for a mixed conductor are described to represent the parallel combination of the electronic resistance and the geometrical capacitance at low frequencies, and the parallel combination of the ionic resistance and the geometrical capacitance at high frequencies. No low-frequency tail can be observed since the interfacial capacitance is shunted by the electronic current at low frequencies. A typical Nyquist plot is shown in Fig. 1(b), and the electronic and ionic resistances can be fitted using the equivalent circuit shown in the inset.

When applying a constant DC polarization to the pellet with ion-blocking electrodes, after reaching the equilibrium the ionic current will be totally blocked, and the residual current is solely from the electronic contribution (I_e). A schematic of current vs. time curve is shown in Fig. 1(c), and the slope of DC voltage V vs. I_e plot represents the electronic resistance of the pellet.

3. Results and discussion

3.1. Phase composition and microstructure

X-ray diffraction patterns of the original powders and sintered pellets are shown in Fig. 2. All the original powders show sharp and well-defined diffraction peaks, indicating their good crystallinity. All the

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