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Characterization of transport properties of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA)

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Abstract

Lithium ion batteries cathode materials with high energy and high power density, along with high safety, excellent cycle life and rate capability are crucial for successfully commercialization of hybrid electric vehicle (HEV) or electric vehicles (EV). One of the promising candidates is Co substituted $LiNiO_2$ (i.e. $LiNi_{1-x}Co_xO_2$ (NC)) due to its favorable capacity (~275mAh/g) and operating cell voltage (4.3V vs. Li/Li^+), which is within the electrolyte stability window. However, this material suffers from poor structural stability upon electrochemical cycling. One of the optimized compositions is $Li_1Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA). The majority of studies have focused on structural characterizations and electrochemical performance tests of the material. The transport properties of the material are still not well understood and only limited information is available in the literature.[1-4] Surprisingly, for NCA there to our knowledge no data that separately provides the electronic and ionic conductivity, only two reports[2,3] on the chemical diffusivity of $LiNi_{1-x}Co_xO_2$ determined by the GITT technique on composite cathodes. The values in these reports are scattered over several orders of magnitude.

Our objective is to determine the electronic and ionic conductivity and diffusivity in phase-pure, additive-free sintered materials using ion- and electron-blocking cell configurations, respectively. Measurements were performed using impedance spectroscopy, direct current (DC) polarization and depolarization techniques, and as a function of temperature and lithium content. NCA exhibits semiconducting behavior at the lithium concentrations studied, in which the electronic conductivity increases with temperature. The increase in electronic conductivity is associated with the presence of mixed valence Ni^{3+}/Ni^{4+} resulting from partial delitiation. It is seen from Fig. 1 that the electronic conductivity increases monotonically with increasing delithiation, with a sharper increase in electronic conductivity after 60 % delithiation. This may be due to the oxidization of a small portion of cobalt ions from trivalent to tetravalent state at this delithiation level.

Lithium ionic conductivity and diffusivity of the fully lithiated phase was measured by AC and DC techniques as a function of temperature (Fig. 2) which provides the activation energy of lithium ionic conductivity (1.15eV) and diffusivity (1.20eV). We also observed a lithium concentration dependence of ionic diffusivity that first gradually decreases with delithiation to 50% delithiation, and thereafter increases with further delithiation. From the results it is concluded that bulk transport of NCA is not rate limiting with respect to use at practical C-rates when micron-scale particles are used.

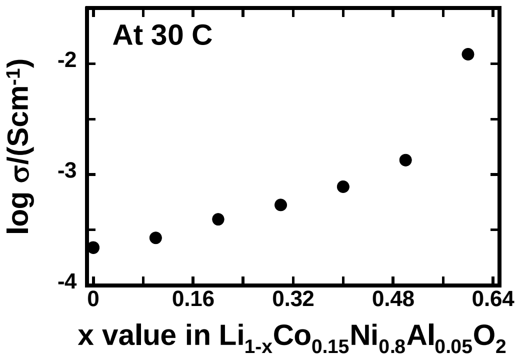

Fig. 1 Electronic conductivity of NCA as a function of lithium content at 30°C.

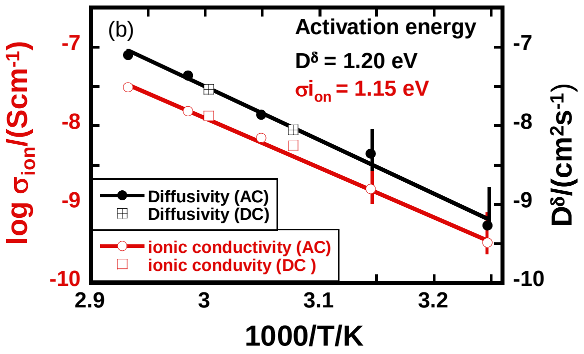

Fig. 2 Ionic conductivity and diffusivity of NCA as a function of temperature.

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