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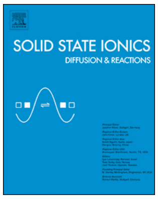

Rational design of a high-energy $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ cathode for Li-ion batteries

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ABSTRACT

The energy density of lithium ion batteries heavily relies on the loading of electrochemically active materials in their cathode. $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) as a promising high-energy cathode material has a practical specific capacity of about 200 mAh g^{-1} which, however, is often compromised by the additives in the electrode, such as the conductive carbon and binder. To harvest a higher energy density NCA electrode, cyclic voltammetry and galvanostatic intermittent titration techniques are employed herein to evaluate the apparent chemical diffusion coefficient of Li^+ and maximize the loading of NCA. Our results show that the carbon content can be reduced to 0.2 wt% (with 97.8 wt% of NCA), making a high-energy cathode for Li-ion batteries. This protocol would also set a precedent for the energy density optimization of other cathodes.

1. Introduction

Having their debut in 1991 by Sony, Li-ion batteries are now dominating the market of portable electronic devices [1]. For common cathode materials of layered LiT_MO_2 (T_M = Ni and/or Co), the solid solutions $LiNi_{1-y}Co_yO_2$ ($0 < y < 1$) normally exhibit improved structure stability with enhanced cycling performance in cell operation as compared to their counterparts with single T_M [2,3]. With a smooth extraction of lithium ions down to $x = 0.25$ ($Li_xNi_{0.8}Co_{0.2}O_2$), as confirmed by *in situ* X-ray diffraction, $LiNi_{0.8}Co_{0.2}O_2$ delivers a high practical specific capacity of ~200 mAh g^{-1} [4,5].

By doping low content of Al into $LiNi_{0.8}Co_{0.2}O_2$, $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) is harvested with further enhanced electrochemical performance. The doped Al^{3+} ions introduce multiple advantages: 1) forming strong O-Al-O bonds to strengthen the crystal structure and hence improves the cycling stability [6]; 2) increasing the electronic conductivity for enhanced cathodic charge transport [7]; 3) expanding the surrounding crystal structure and giving NCA (a = 2.87 Å, c = 14.20 Å) a larger lattice size (compared to its counterpart $LiCoO_2$ with a = 2.82 Å, c = 14.09 Å) [8] for higher Li^+ mobility. Particularly, Li^+ ions in the layered cathode moving along the direction perpendicular to c axis (elongated in NCA), are hence faster which enables a higher ionic conductivity [9–11]. These merits have made NCA an important cathode material with successful adoptions in batteries for electric vehicles [12–14].

The electronic conductivity of an electrode is equally important. It determines the rate of charge transfer between electrochemical reactions at the cathode and the external electrical circuit. The pristine electronic conductivity of NCA at room temperature is ~10^{-4} S cm^{-1}, and will increase to 10^{-3} S cm^{-1} after delithiation to form $Li_{0.5}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ in charge process [15]. To achieve good rate performance in NCA-based batteries, the electronic conductivity of the electrode must be improved, *e.g.* by incorporating conductive carbons [16]. Nevertheless, carbon incorporation may bring along some adverse impacts. Firstly, loose carbon granules tend to make the electrode fragile and hence require more polymer binder to ensure the electrode integrity; Secondly, excessive carbon affects the ionic conductivity, particularly for olivine-type of cathodes with an ultralow Li^+ diffusion coefficient (*e.g.* $LiFePO_4$) [17]. To achieve high energy density, it is essential to minimize the use of inactive materials (conductive carbon and binder), while ensure the electrical conductivity and the structural integrity of the cathode [18].

In this work, we determine the apparent chemical diffusion coefficient of lithium ions ($D_{Li^+}^{app}$) in $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) by cyclic voltammetry (CV) and galvanostatic intermittent titration technique (GITT) analyses, and use the results as criteria to optimize the ratio of NCA to conductive carbon. We demonstrate a high energy density cathode with an NCA content of 97.8 wt% (much higher than the

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commonly reported value of 88 wt%) [18] and only 0.2 wt% conductive carbon.

2. Experimental

NCA cathode powders (D_{50}: 14.0 μm) were purchased from BTR New Energy Materials Inc. Denka black and polyvinylidene difluoride (PVDF, Solef® 5130) were the conductive additive and binder, respectively. Dispersion of single-walled carbon nanotubes (SWCNTs) in *N*-methyl-2-pyrrolidone (NMP, 0.1 wt% SWCNTs in NMP) was sponsored by OCSiAl. All materials were used as received without further treatment. The electrode slurry was prepared from NCA, conductive carbon (either Denka black or SWCNTs) and PVDF with predetermined weight ratios in NMP (anhydrous, 99.5%, Sigma-Aldrich) using a mixer (Thinky, ARE-310), before being evenly cast on Al foil and dried at 80 °C prior to roll pressing. Typically, the cathode consists of NCA, Denka black and PVDF at 90, 5 and 5 wt%, respectively, with an areal NCA loading of 10 ± 0.5 mg cm^{-2} (Φ = 12.7 mm). Electrochemical performance was evaluated in CR2032 coin cells with a Celgard separator and lithium anode (Φ = 15.8 mm), assembled in an Ar-filled glove box (MBraun, H_2O < 0.1 ppm, O_2 < 0.1 ppm). The electrolyte was 1 M $LiPF_6$ dissolved in ethylene carbon and ethyl methyl carbonate (1:1, v/v, Aldrich, H_2O level: 22.3 ppm, determined by Mettler Toledo C20X Karl Fisher titrator). The cells were cycled between 2.8 and 4.3 V (*vs.* Li/Li$^+$) at a constant current on a Neware battery testing system. CV and GITT tests were conducted on a Metrohm Autolab potentiostat/galvanostat. Powder X-ray diffraction (XRD) pattern was recorded by a Bruker D8 advance with Cu Kα radiation (λ = 1.5406 Å). Scanning electron microscope (SEM) images were taken on a field-emission SEM (JEOL JSM-7600 field-emission) with an accelerating voltage of 5 kV.

3. Results and discussion

XRD pattern (Fig. 1a) suggests a layered α-$NaFeO_2$-type structure (space group: *R-3m*) for the obtained NCA, and the high intensity ratio of $I_{(003)}/I_{(104)}$ (> 2.1) indicates a low degree of cation disorder [19]. Based on the peak positions, the lattice parameters are calculated to be a = 2.865 Å and c = 14.169 Å, which will be used to determine the cell volume in the following study. When coupled with lithium anode, the NCA cathode delivered a reversible capacity of 210 mAh g^{-1} at 0.1C with the initial Coulombic efficiency of 93.8% (Fig. 1b). The good cycling performance enables CV and GITT measurements to determine the apparent chemical diffusion coefficient of lithium ions (D_{Li+}^{app}) in $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$.

CV curves of the NCA cell are shown in Fig. 2a, with the scan rates being 0.06, 0.1, 0.15 and 0.2 mV s^{-1}, respectively. Three couples of redox peaks (Ox1/Red3, Ox2/Red2, and Ox3/Red1) are easily identifiable. At higher scan rate, the oxidation peaks shift to higher voltage with the peak current increases following the classical *Randle-Sevcik* equation [20]:

$$I_p = 0.4463 n^{3/2} FA\, f^{1/2}\, C_{Li}{}^{*}\, \nu^{1/2}\, D^{app}{}_{Li+}{}^{1/2} \tag{1}$$

where I_p is the peak current (A), n the charge transfer number (equal to 1), F the Faraday constant (96,485 C mol^{-1}), A the geometric electrode area (1.27 cm^2), $f = F / RT$ (R, the gas constant; T, the absolute temperature), C_{Li^*} the bulk concentration of lithium ions in the electrode (mol cm^{-3}, varying with the charge/discharge state), ν the scan rate (V s^{-1}) and D_{Li+}^{app} the apparent chemical diffusion coefficient of lithium ions in $Li_xNi_{0.8}Co_{0.15}Al_{0.05}O_2$. According to Eq. (1), I_p is linear to the square root of scan rate (Fig. 2b). C_{Li^*} for each red-ox peak is calculated from the lattice parameters which are derived from XRD data and the charge/discharge capacity. The little volume expansion of NCA in delithiation (~2%) is neglected for simplicity [8]. The obtained C_{Li^*} and D_{Li+}^{app} are summarized in Table 1. For the first oxidation peak (Ox1), D_{Li+}^{app} is 1.49 × 10^{-9} cm^2 s^{-1}. At higher voltages more lithium vacancies are generated, which facilitates Li$^+$ diffusion and hence gives larger D_{Li+}^{app} of 8.63 × 10^{-9} cm^2 s^{-1} at Ox2 and 2.29 × 10^{-8} cm^2 s^{-1} at Ox3. In the following discharge process, D_{Li+}^{app} decreases from 2.82 × 10^{-8} cm^2 s^{-1} (at Red1) to 5.14 × 10^{-9} cm^2 s^{-1} (at Red3) as occupancy of lithium ions makes the further insertion slightly more difficult. Hence, for NCA in a full charge-discharge cycle, D_{Li+}^{app} fluctuates in the range of 10^{-9} to 10^{-8} cm^2 s^{-1}.

To obtain the specific D_{Li+}^{app} at each stage of cell operation, GITT analysis was employed to allow the cell to be progressively pulsed at a constant current of 18 mA g^{-1} for 30 min, followed by a relaxation of 30 min (Fig. 2c). The cell voltage could reach equilibrium in < 5 min during each break as shown in the curve of voltage change *vs.* relaxation time (the inset of Fig. 2c). Prior to the GITT measurement, the cell was cycled for 5 times at 0.1 C for stabilization. D_{Li+}^{app} for each pulse can be derived from:

$$D_{Li^+}^{app} = \frac{4}{\pi}\left(\frac{iV_m}{nFA}\right)^2 \left[\left({}^{dE}\!/_{dx}\right)\Big/\left({}^{dE}\!/_{dt^{1/2}}\right)\right]^2 \tag{2}$$

Here, i is the applied pulsed current (A), V_m the molar volume of NCA (20.2 cm^3 mol^{-1}). dE/dx is the slope of charge/discharge voltage *vs.* x in $Li_xNi_{0.8}Co_{0.15}Al_{0.05}O_2$ and $dE/dt^{1/2}$ represents the slope of the linearized plot of voltage change *vs.* the square root of relaxation time (in the first 25 s). The derived D_{Li+}^{app} values were plotted against x in $Li_xNi_{0.8}Co_{0.15}Al_{0.05}O_2$, as shown in Fig. 2d.

As the cell was discharged from 4.3 to 4.0 V, D_{Li+}^{app} sharply increases by 4 orders of magnitude from 3.46 × 10^{-13} (x = 0.26) to 1.68 × 10^{-9} cm^2 s^{-1} (x = 0.42). At the voltage below 4.0 V D_{Li+}^{app} slightly varies with x in the range of 10^{-9} to 10^{-8} cm^2 s^{-1}, showing a M-shaped curve with a minima of 1.08 × 10^{-9} cm^2 s^{-1} at x = 0.68. The presence of a "lowest" ionic diffusivity at x = 0.68 was also observed for $Li_xNi_{0.8}Co_{0.2}O_2$ previously [21], attributed to the formation

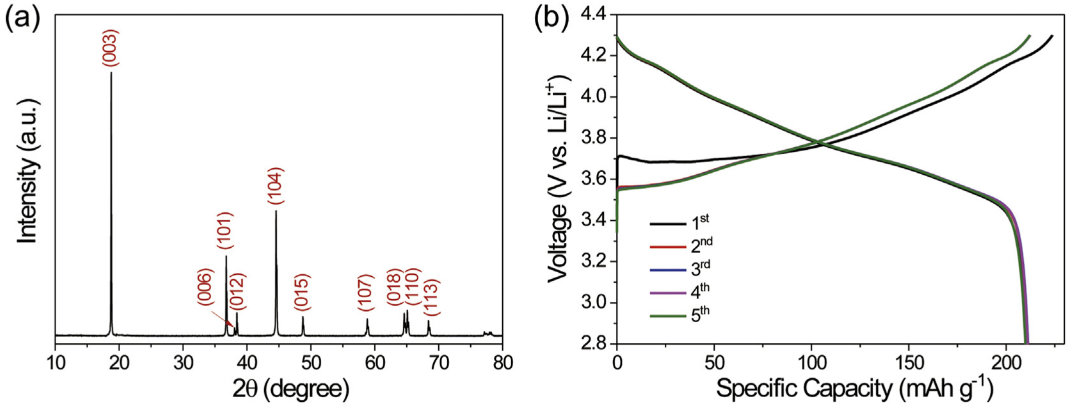

Fig. 1. (a) XRD pattern of the NCA powders from BTR and (b) galvanostatic charge-discharge profiles for the first 5 cycles at a rate of 0.1 C.