Kinetic characteristics up to 4.8 V of layered $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode materials for high voltage lithium-ion batteries

Xianhui Zhang^{a,b}, Zhenlian Chen^{*a}, Björn Schwarz^c, Florian Sigel^c, Helmut Ehrenberg^{c,d}, Ke An^e,
Zhifeng Zhang^{a,b}, Qinggang Zhang^f, Yantu Li^f, and Jun Li^{*a}

Abstract

Understanding the structure properties in deep delithiated states and electrochemical kinetics in the high potential window of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NCM) cathode materials is essential to advance their performance in rechargeable lithium-ion batteries for 5 V chemistry. Here we report a layered single-phase NCM showing great structural reversibility and without H3 phase formation when charged up to 4.8 V at least for 5 cycles. However, the poor cluster scale conductivity results in inactive material in thick electrode during cycling, approximately 10% (w/w), may corresponding to the reduced capacity respective to thin electrode. The $\text{Co}^{3+}/\text{Co}^{4+}$ redox peaks are found clear and stable for cycles, lying between 4.5~5.0 V. That is tightly correlated to the fast Li-ion kinetic, i.e., the electrochemical behaviour of the NCM material is not limited by Li^+ diffusion but behaving like in a thin layer. That is very different from previously reports on charge transfer mechanisms of cathode materials for lithium-ion batteries.

Keywords: $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$; Structure reversibility; Electrochemical kinetics; Redox couples; Lithium-ion battery

1. Introduction

Transition metal (*TM*) layered oxide $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NCM) is one of the most attractive cathode materials due to their high capacities ($> 200 \text{ mAh g}^{-1}$) applicable to 5 V lithium chemistry.[1] Extensive studies have been executed trying to identify the key factor in materials properties determining such capacity above 4.4 V for NCM.[2-7] However, the intrinsic kinetic behaviors, which are critical

electrochemical properties limiting their battery performance, have not been depicted clearly.[7-9] The electronic and ionic conductivities within the electrode architecture are well known to tightly contact with the electrochemical reaction kinetics and rate capabilities. The power performance of the LiFePO_4 , for example, is always limited by its low intrinsic electronic conductivity. For NCM cathode, the conductivity is hardly the dominant factor according to previous reports. While, *Seid* et al. have demonstrated that within NCM material, the clusters of particles bring boundaries, junctions and interfaces.[10, 11] This will result in various polarizations ranging from interatomic distances to macroscopic sizes, leading to the conductivity is different in multiscale. The multiscale conductivities should be taken in account when exploring the intrinsic kinetic properties.

Kinetics of lithium intercalation/deintercalation affect both redox reactions and structural evolutions for NCM. Ceder et al. suggested that the electrochemical performance of NCM may critically depend on the stable ground state of $\text{Co}^{3+}/\text{Co}^{4+}$ redox couple in high voltage region, which determines the reversible capacity for lithium concentration range $2/3 \leq x \leq 1$ for the $\text{Li}_{1-x}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, i.e., relating to usable capacity above 185 mAh g⁻¹. [12] Shaju et al. identified that the redox processes at 4.65~4.55 V can be assigned to $\text{Co}^{3+}/\text{Co}^{4+}$ couple in NCM.[13] This is different from that of in LiCoO_2 , where the $\text{Co}^{3+}/\text{Co}^{4+}$ redox potential is reported to be mainly around 4.11 V plus a second, unstable redox pair at 4.58 V.[14] The latter pair is attributed to the formation of Jahn-Teller low spin d ions according to Ohzuku and Ueda.[15] A very surprising observation in previous studies of NCM materials is that while many works have reported more than 200 mAh g⁻¹ capacity when cut-off

voltages increased above 4.6/4.8 V, the $\text{Co}^{3+}/\text{Co}^{4+}$ redox couples became diminishing or even absent.[5, 16, 17] Therefore, new experimental evidence is needed to clarify the mechanism for a stable and reversible redox reaction above 4.5 V and whether or not it is based on new structural phase or the intrinsic redox potential of Co^{3+} . Furthermore, it is well-known that the layered lattice is difficult to stay stable above 4.4 V in deeply delithiated states, which is assumedly a major material deficiency leading to electrochemical degradation in all kinds of layered oxides including NCM. [18, 19] Yin et al. found the formation of an O1 phase (trigonal;) upon deep delithiation is responsible for the serious deterioration of cyclability in the region above 4.4 V.[20] Mohanty et al. observed layered to spinel phase transition following Li^+ deintercalation in NCM, which would result in capacity-fading in cycling.[21] Unfortunately, phase stability of ternary Ni-Mn-Co oxide family seems to depend on the material preparation, making careful data comparison more difficult.[22, 23]

In this work, we present clear experimental data with careful analysis to understand the structural and electrochemical kinetics of NCM material for 5 V chemistry. We combine *ex/in situ* synchrotron X-ray and neutron powder diffraction to characterize a well-prepared single-phase NCM. Special attention has been paid on the structural evolution during cycling in voltage range of 2.8-4.8 V. Thin and thick electrodes are compared to clarify the connection between the inactive materials and the multiscale conductivity. Comprehensive kinetic mechanisms in the full charge/discharge process are decisively determined by cyclic voltammetry and analyzed by diffusive models with thin and thick electrodes. To our best knowledge, there are still no literatures discussing the charge transfer mechanism related to Co in the potential

window up to 4.8 V. These fundamental insights of the complex kinetic mechanisms may contribute to the development of advanced cathode materials for 5 V chemistry.

2. Experimental Section

2.1. Sample preparation

$\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}(\text{OH})_2$ precursors were synthesized by the coprecipitation method. $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ were dissolved in di-ionic water at 1:1:1 ratio in mole. 1 M NaOH was pumped into the continuous stirring reactor with Ni-Co-Mn aqueous solution to prepare $\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}(\text{OH})_2$ precursors. All chemicals were purchased from Aldrich. No chelating agents or others like formaldehyde were used in the material processing. $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NCM) samples were prepared with high temperature solid-state method. The prepared $\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}(\text{OH})_2$ were mixed with $\text{LiOH} \cdot \text{H}_2\text{O}$ (Aldrich, Analytical reagent) at a molar ratio of 1:1.05 by roller milling for 9 h. Then, the mixed powders were subjected to heat treatment at 400 °C for 8 h and further calcination at 900 °C for 12 h in air. After automatically cooled to room temperature, the samples were stored in desiccator for investigation.

2.2. Sample analysis

Morphology was observed with an S-4800 Field Emission Scanning Electron Microscope (FESEM, Hitachi S-4800, Ltd., Japan). The accelerate voltage used here was 8 kV. The elemental compositions were characterized using the energy dispersive spectroscopy (EDS). The particle size distribution was tested with Microtrac Particle Size Analyzer (S3500-special, Microtrac, USA). Brunauer Emmett Teller (BET) surface area was measured with a Micromeritics Instruments ASAP 2020M.

2.3. Synchrotron diffraction (XRD)

The synchrotron diffraction experiments have been performed at beamline P02.1[24] at the synchrotron facility DESY (Petra III) in Hamburg, Germany. The wavelength of 0.2076 Å corresponds to high photon energy of approximately 60 keV. A 2D CCD detector (Perkin Elmer) with 2048×2048 pixels was used for the data acquisition. The system calibration and 2D-image integration was performed with the software FIT 2D (Dr. Andy Hammersley, ESRF). The sample has been measured within a custom made *in situ* coin cell attached to a custom made 8-fold sample holder.[25] A synchrotron diffraction pattern has been measured approximately every ten minutes for an exposure time of about 30 seconds each. A dark image to correct for detector artefacts has been recorded before each diffraction pattern at the same measuring time. The Rietveld refinement was carried out using the software package FullProf.[26] The peak profile shape was described by a pseudo-Voigt function (profile function 7). The halfwidth (Caglioti) parameters were refined using a LaB₆, respectively a Si-, standard sample.

2.4. Neutron Diffraction (ND)

The neutron powder diffraction measurements were conducted at the VULCAN instrument at the most intense Spallation Neutron Source, Oak Ridge National Laboratory.[27] The powders were sealed in 6.35 mm in diameter cylindrical vanadium can. A gauge volume of 5×12×5 mm³ is determined by the incident slits and the 5 mm radial collimators. The measurable d-spacing range is 0.05-0.35 nm. The neutron data was collected under high resolution mode for about 4 hours. The data was reduced by VDRIVE software. The structural information are analyzed by

Rietveld refinement using GSAS.[28]

2.5. Electrochemical measurement

For the test cell, the working electrodes were fabricated by mixing 85:10:5 (w/w) ratio of NCM materials, super P carbon and polyvinylidene fluoride in N-Methyl-Pyrrolidone with stirring for 2 h. The resulting slurry was cast on an Al current collector, followed by drying at 120 °C for 12 h under vacuum oven. The electrode foils were subsequently pressed and punched into $\phi 14$ mm disks. Then, CR 2032 coin-type half-cells were assembled using Celgard 2550[®] as separator, lithium foil as anode, and 1 M solution of LiPF₆ in ethylene carbonate/ dimethyl carbonate (EC/ DMC, 1:1 by volume) as electrolyte. The assembly of the test cells was performed in an Ar-filled M-Braun glove box with water and oxygen contents less than 1 ppm. Electrochemical performances were evaluated on Land CT2001C battery testers (Wuhan, China) between 2.8 and 4.8 V *vs.* Li/Li⁺ at 25 °C. In this work, 1 C was defined as 180 mAh g⁻¹. Cyclic voltammograms (CVs) were measured using SI 1470 (Solartron Analytical, Cambridge, UK) with different scan rates between 2.0 and 5.0 V *vs.* Li/Li⁺ at 25 °C. The conductivities of the NCM pristine powder and composite electrodes were characterized with Four-Point Probe Meter (CRESBOX, NAPSON, Japan).

3. Results and discussion

A typical X-ray diffraction pattern of the NCM sample is shown in **Figure 1a**. All peaks are indexed based on the α -NaFeO₂ structure, showing high quality crystalline features of, which are further confirmed by the neutron diffraction (ND) pattern presented in Figure 1b. The integrated intensity ratios of 003 to 104 is

observed to be 1.04(3) in Figure 1a (Obtained in the case of excluding the interference of preferred orientation), which is larger than 0.8 determined by Shaju et al.[13]. This means the as-prepared NCM sample has less Li/Ni cation mixing compared to that in Shaju et al.'s work, indicating potential differences in electrochemical properties.[29, 30] The 006/102 and 108/110 reflections are observed to be clearly separated in the XRD pattern. These separations are characteristic of the layered structure, with rhombohedral distortion of the oxygen sub lattice from a close packed *fcc* array. The as-prepared NCM has a *c/a* ratio of 4.974(1) by Rietveld refinement, which is well above the typical value of 4.899 (when the distortion in the *c* direction is absent), i.e. the layered structure is formed with a clear rhombohedral distortion. This is different from the layered $\text{Li}_{1+\delta}(\text{Mn}_x\text{Ni}_{1-x})_{1-\delta}\text{O}_2$ system, where the reflections 108/110 etc. superimpose.[31, 32] The origin of this distinction could attribute to the addition of Co to $\text{LiMn}_{1-y}\text{Ni}_y\text{O}_2$ according to Ohzuku et al., and they reported that the presence of Co would reduce Li/Ni cation mixing and stabilize the layered structure, corresponding to distortion of the oxygen sub lattice with expansion of the *c* axis accompanied by an increasing degree of the splitting of 006/102 and 108/110 reflections.[33, 34] The influence of Co after invoking in NCM may also depress phase separation compared to $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ as reported by Dahn et al. which shows greater signs of phase separation into layered-layered composites with the same synthesis condition of the as-prepared NCM.[31]

For Rietveld refinement, based on the synchrotron and neutron powder diffraction patterns, the space group structural model that incorporates Li/Ni site intermixing: beginning with a full occupation with Li on the 3b site (Li-layer), a 1/3

occupation with Ni, Co and Mn, each, on the 3a site (*TM*-layer) and a full occupation with oxygen on the 6c site, the structural model allows for Li/Ni exchange between the Li- and the *TM*-layer while maintaining a full occupation of all these crystallographic sites. The simple random distribution model with space group is found as a better fit to the ND pattern as well as to XRD than the superstructure model with space group $P3_1I2$.^[20] The results of the Rietveld refinement with the calculated and observed intensities together with the difference plots are shown in Figure 1a and 1b. **Table 1** summarizes the structural parameters obtained from the neutron Rietveld refinement. The lattice parameters refined to $a = 2.86243(1)$ and $c = 14.23776(1)$ (with c/a ratio 4.974(1)), and the refined density is 4.77 g cm⁻³, Reduced $\chi^2 = 2.19$, which are within the limit characteristics for this type of material.[20, 35] The degree of Li/Ni cation disordering is determined to 3.0(1)% for the neutron case, i.e. similar to those values reported previously.[2, 13, 36]

Figure 2a shows scanning electron microscopy (SEM) images of the as-prepared NCM material at low and high magnifications, respectively. The investigated samples exhibit relatively uniform primary particle sizes of about 200~400 nm with potato-like morphologies and only a small amount of the primary particles are formed into larger loose agglomerates. Herein, the as-prepared material yields an optimized surface-area value of 4.2 m² g⁻¹ by BET measurement, which is smaller than nano-scaled particulate materials [37, 38], and different from macroporous morphologies previously reported [2, 6]. The elemental distribution mappings of Ni, Co, Mn and O in Figure 2b reveal that all of the metal elements are well distributed throughout the NCM sample. As shown in Figure 2c, the D_{50} , D_{80} and D_{95} values of the NCM

particle size distribution are $\sim 1.813\ \mu\text{m}$, $\sim 7.64\ \mu\text{m}$ and $\sim 17.58\ \mu\text{m}$, respectively, consistent with the SEM characterizations.

To track the crystal structure evolutions during cycling at high cut-off voltages, we performed *in situ* synchrotron diffraction during the first initial two full cycles between 2.8 V and 4.8 V. As shown in **Figure 3a**, overall 136 diffraction patterns had been measured during the whole in operando experiment. Note that even though the electrode had a high mass loading of active material up to $4.802\ \text{mg cm}^{-2}$, its signal is still weak compared to those of Al from the current collector and Li foil from the counter electrode. During the first charging, the 003 reflection continuously shifts to lower scattering angles and then to the higher, corresponding to expansion and then contraction of the *c*-lattice upon the removal of the lithium ion; during the later discharge process, it follows the same behaviour.[18, 39] However, different from previous *in situ* XRD, it is obvious that the reflections evolution for the first two cycles is almost identical, exhibiting great structural reversibility. Figure 3b presents a direct comparison of the first (pristine material) and the last diffraction pattern (discharged to 2.8 V after two full cycles), there are almost no obvious differences in shapes and intensities, and no peak shift or new peak of phase separation has been observed. Figure 3c presents the evolutions of lattice parameters *a*, *c*, unit cell volume *V*, *c/a* ratio and EC curve vs. the number of diffraction patterns of the electrode material as a result of the Rietveld refinement. It is found that the deviations of *a*, *c* and *V* between the end of the first and second cycle are almost vanished, corresponding to the same intercalated state. After two full cycles between 2.8 V and 4.8 V, the parameter *a* contracts by 0.08% and parameter *c* expands by 0.46%,

resulting in almost no change of the unit cell volume V when compared to that of pristine NCM material. This data confirms that the NCM materials can conserve high stable layered lattice structure even in very deep deintercalated states. This is different from the observations by Kim et al.. In their work, deeply delithiated NCM underwent a phase transition from layered phase to spinel cubic structure.[40] Previous works often suggested surface treatment may help improve materials stability. Our experiment indicates that while chelating agents like ammonia or others like formaldehyde may help formation of secondary particles, their side effects may erode layered lattice and harm the surface layers of NCM. However, the detailed correlation needs further dedicated study in future.

In layered LiMO_2 ($M=\text{Ni, Co, Mn, Ti, etc.}$) systems, the formation of additional hexagonal phases is always believed to be a key indicator of poor structural and thermal stability.[18, 19] Shu et al. found that the suppression of the formation of a third hexagonal phase (called H3) can achieve a long-term cycability and high reversible capacity for $\text{LiNi}_{0.5}\text{Co}_{0.3}\text{Mn}_{0.2}\text{O}_2$. [39] Yoon et al. reported that the $\text{Li}_{1-x}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ material having better H3 phase suppression and a smaller 003_{H3} shoulder than that of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA) results in superior thermal stability and better structural reversibility for a longer cycling life.[18] Surprisingly, as shown in Figure 3a, there is no signature of this typical shoulder feature of H3 as always observed in other *in situ* XRD works, when the NCM electrode was charged to 4.8 V. The H3 phase formation even occurred in LiNiO_2 at the low voltage of 4.3 V.[19] This may partly explain the superior thermal stability at deep-charged states of the NCM over high Ni-concentrated materials including NCA and LiNiO_2 . The very small cell

parameters variation and nearly zero change in unit cell volume as well as no phase transition during cycling provide a high quality NCM sample for understanding its intrinsic electrochemical kinetics.[18]

It is very surprising that a small portion of the NCM materials is electrochemically inactive in the voltage window between 2.8 and 4.8 V during cycles. As shown in **Figure 4a**, diffraction patterns Nr. 24 and Nr. 40, for example (see Figure 3c for assignment of number of diffraction pattern to electrochemical state), exhibit weak contributions of additional reflections, which can be explained by a certain part of cathode material that did not take part in electrochemical cycling. In other words, there is a small fraction of inactive particles in the electrode during charging and discharging with the lattice parameters of the pristine material, indicating that not all NCM particles are active in the tested-thick electrode. To estimate the fraction of inactive particles, Rietveld refinement to the *in situ* diffraction pattern Nr. 24 was performed, applying two phases as electrode material, one phase with constant lattice parameters as determined for the pristine material, as shown in Figure 4b. The quantitative analysis reveals that approximately 10% (w/w) of the electrode material does not change lattice parameters during electrochemical cycling, i.e. is supposed to be inactive. Li et al. have demonstrated that the particles near the carbon network will be (de)lithiated preferentially, which implies that the lithiation/delithiation suffers strong conductivity limitation.[41] We have measured the conductivities of the NCM pristine powder and composite electrodes with various carbon black contents. The conductivity is 0.161 S m^{-1} when 5 wt.% carbon black is introduced, which is five orders of magnitude higher than that for pristine NCM

($1.57 \times 10^{-6} \text{ S m}^{-1}$), and then gradually rises to 2.28 S m^{-1} for 25 wt.% conductive additive. It suggests the percolation threshold of carbon black is no larger than 5 wt.% for NCM cathode, and proves the important of carbon black in reducing conductivity limitation. The multiscale conductivities in materials are relate to the multiscale electric polarizations. Seid et al. have reported that the conductivity drop from the primary particle to the cluster scale is comparatively large in NCM, owing to the presence of amorphous grain boundaries between the particles within the clusters.[10] For the clusters of the NCM sample in which the primary particles are loosely stacked, the grain boundaries will be more, and then the drop will be larger. As the polarization is additive, the larger the size of cluster, the greater the polarization, accordingly, the poorer the conductivity. We infer it is the poor conductivity at the clusters scale, especially the large ones, which makes the particles within the clusters are failed to (de)lithiate at the given rate, i.e. be inert.

To clarify the correlation between multiscale conductivities and lithiation/delithiation performance of the tested materials, thin and thick electrodes are employed. We analyze the active material limitation on discharge capacity through varying the electrode loadings from 0.61 mg cm^{-2} to $14.193 \text{ mg cm}^{-2}$. The 1st cycle discharge capacity as a function of the electrode loading for NCM electrodes at 36 mA g^{-1} in the voltage window of 2.8-4.8 V are shown in Fig. 5a. The curve indicates that before the electrode loading increase to 1.909 mg cm^{-2} , there is a linear relationship between capacity and mass loading; and start from 1.909 mg cm^{-2} , the discharge capacity keeps almost constant around 222 mAh g^{-1} . It suggests that the active material limitation would be ineffective when the electrodes are thick enough.

Accordingly, two electrodes gives an electrode loading of 0.61 mg cm⁻² and 3.83 mg cm⁻², which corresponding to a cathode thickness (have subtracted the thickness of the current collector) of 8 μm and 41 μm, respectively, are employed. The particle size distribution results show that 80% NCM particles is smaller than 7.64 μm and 95% NCM particles is smaller than 17.58 μm. With a cathode thickness of 8 μm, the clusters larger than 8 μm, in which the inner particles are probably inactive, have the potential to be screened out. The smaller the clusters, the less the polarization, and the better the conductivity. This could lead to the particles be well connected in the electrode, resulting in more involvement of particles, smaller inherent resistances and less transport loss, which all will contribute to a higher specific capacity and less polarization for the thin electrode compared to the thick one. As shown in **Figure 5b**, the charge/discharge curves were measured at 36 mA g⁻¹ on the thin and thick NCM electrodes, in the voltage windows of 2.8-4.8 V. For the thin electrode, the first two charge/discharge capacities are up to 291.7/238.2 mAh g⁻¹ (the extra initial charging capacity may be from the side-reaction of electrolyte and corresponding SEI film on the electrodes in the high potential range[5, 7]) and 256.4/238.2 mAh g⁻¹, respectively. It is worth noting that the discharge capacity of the second cycle is close to that of the first one. For the thick electrode, the first two charge/discharge capacities are 261.4/222.5 mAh g⁻¹ and 225.9/215.8 mAh g⁻¹, respectively. Interestingly, about 10% more specific charge/discharge capacities and higher discharging platform are shown in the thin electrode compared to the thick electrode. It indicates that the conductivity at cluster scale strongly limits the electrochemical performance of NCM materials, and is responsible for the 10% (w/w) inactive

material.

According to the above results, the thin electrode employs less polarization, and thus better conductivity. We suppose that in a thin electrode, the conductivity corresponds to the intrinsic conductivity of NCM. Without the interference of structural transformation, intrinsic kinetic properties in high potential region were measured using cyclic voltammetry (CV) with thin electrodes. The characteristic shapes of the CV curves and their unequivocal positions on the potential scale virtually fingerprint the individual electrochemical properties of redox systems. **Figure 6** compares CV characterizations of both the thick and thin NCM electrodes at various scan rates in the potential window of 2.0-5.0 V. Remarkably, oxidation/reduction peaks of the $\text{Co}^{3+}/\text{Co}^{4+}$ couple lying between 4.4~5.0 V are found clear and stable for the cycles with different scan rates. That is rarely reported in literature, even when the cut-off potentials of electrochemical tests are above 4.5 V.[16, 17, 20] This observation suggests a higher electrochemical redox reaction activity of the NCM sample and confirms the charge/discharge capacity of more than 200 mAh g⁻¹ with considerable contribution from $\text{Co}^{3+}/\text{Co}^{4+}$ redox reaction.[5, 42] The oxidation potentials ($\text{Ni}^{2+}/\text{Ni}^{4+}$ as well as $\text{Co}^{3+}/\text{Co}^{4+}$) in the second cycle shift to smaller values with respect to the first one for most scan rates and more profound as the scan rate increased, except for a mediate rate of 0.5 mV s⁻¹. After the second cycle, the following cycles are highly repeatable, indicating stabilization of the NCM electrode.

Table 2 summarizes the redox peak positions and potential intervals ΔV_s (the peak separation between anodic and cathodic peaks) for the thick and thin NCM electrodes at a scan rate of 0.1 mV s⁻¹ from Figure 6a and 6b. The ΔV_s of the thin

electrode are smaller compared to the thick electrode and the potential deviation between the first and second cycle is smaller in the thin electrode. These observations are consistent with the charge/discharge behaviors in Figure 5, confirming the effect of kinetic properties on the electrochemical performances. In the thin electrode, the potential difference between the first pair of anodic and cathodic peaks is 0.13 V. This value is much smaller than previous result of about 0.34 V.[6] The reduced electrode polarization is probably due to the considerable connectivity in the thin electrode, but differences of other fabrication factors such as electrode thicknesses, packing densities may also matter. In the second cycle the value for the $\text{Ni}^{4+}/\text{Ni}^{2+}$ couple decreases to 0.095 V and almost remains constant in the following cycles. For the $\text{Co}^{3+}/\text{Co}^{4+}$ couple above 4.5 V, the ΔV_s is 0.061 V in the first cycle, which is less than half of the value of LiCoO_2 tested by Xia et al.[43], and further decreases to 0.031 V in the second cycle before increasing back to 0.061 V in the fifth cycle. These values are close to the theoretical value 0.059 V for the ideal reversible electrode, which benefits the fast charge transfer kinetic in the high voltage range.

To further explore the kinetic properties in high voltage range, kinetic analyses of the NCM electrochemical behavior based on CV results have been performed. For Li^+ kinetic behavior, the peak current I_p (A) is reported to follow a power law relationship with the sweep rate ν (V s^{-1}) [44]:

$$I_p = a\nu^b \quad (1)$$

where a and b are adjustable parameters, and b would provide insight with regard to the charge transfer mechanism. When the b -exponent is ~ 0.5 , meaning the charge transfer is controlled by semi-infinite linear diffusion, which is often obtained in

lithium-ion batteries; a value of 1 indicates surface-controlled, which is typical for a supercapacitor.[44] Based on Equation (1), a plot of $\log(I_p)$ versus $\log(v)$ for both the cathodic and anodic peaks is shown in **Figure 7**, to explore the intrinsic kinetic mechanisms of NCM including both the $\text{Ni}^{2+}/\text{Ni}^{4+}$ and $\text{Co}^{3+}/\text{Co}^{4+}$ redox couples. For sweep rates ranging from 0.02 to 5 mV s^{-1} (0.02, 0.05, 0.1, 0.2, 0.5, 1, 2, 5 mV s^{-1}), the b -value for both the cathodic and anodic peaks is close to 1.0 instead of 0.5 (see **Table 3**). These values in current battery system indicate that the Li^+ transfer is not dominated by a solid-state diffusion-controlled intercalation mechanism and may behave like in a thin layer[45]: The lithiation/delithiation occur in the entire bulk of the materials, i.e. no inactive particle, and all the oxidation/reduction sites participate to the process, enabled by a fast mobility of Li^+ ions without concentration gradient, which probably benefits from the better particle connectivity in the thin electrode (much less clusters than the thick electrode). This is consistent with the electrochemical performances and CVs. Furthermore, the values of b in each charge/discharge states are different, which are conjectured to imply different proportion of the active particles in electrode materials during cycles. And this deviation potentially arises from the different Li contents and Ni valence states within the lithiation/delithiation processes according to the studies of Wei et al..[8] It is obvious that the use of a varying kinetic parameter is necessary for studying the transport processes in NCM. The exact contribution of v and $v^{1/2}$ to the total measured current in the full charge/discharge range and the complex relationship between electrochemical kinetic and active particle population need to be determined in the future studies.

Nevertheless, in most intercalation materials charge transfer is reported to be

limited by solid-state diffusion and therefore the peak currents scale with $\nu^{1/2}$. We also tried to fit the relationship between the I_p and $\nu^{1/2}$ in the full redox processes for sweep rates ranging from 0.02 to 5 mV s⁻¹, as shown in **Figure 8**. It is found that the charge transfer process hardly follows the same kinetic behaviors depending on the scan rate as previously reported [16, 17], but splits into two regimes at 0.5 mV s⁻¹, marked as (a) and (b). We evaluated the diffusion coefficient of Li-ions based on the Randles–Sevcik equation[16]:

$$I_p = 2.69 \times 10^5 n^{3/2} A (D_{Li^+})^{1/2} C_{Li^+} \nu^{1/2} \quad (25^\circ C) \quad (2)$$

where I_p is the peak current (A); n is the number of electrons per reaction species; A is the electrode area (cm²); D_{Li^+} is the diffusion coefficient (cm² s⁻¹); ν is the scan rate (V s⁻¹); and C_{Li^+} is the change of lithium concentration in the related reactions (mol cm⁻³). Accordingly, lithium ion diffusion values can be calculated by Equation (2) from the slope of $dI_p/d\nu^{1/2}$. The evaluated Li⁺ diffusion coefficients are shown in **Table 4**. In fact, the evaluated value should be smaller than the actual coefficient because the limiting step is not the Li⁺ diffusion. One can see that the coefficient derived from b-regime is higher than a-regime. That is different from the Li⁺ kinetic behavior reported by Augustyn et al., where the solid diffusion of Li⁺ is the limiting step of the kinetic reaction at high scan rate.[44] In addition, the evaluated diffusion constants for both Li⁺ insertion and extraction are almost two or three orders larger than previous studies[16], where the D_{Li^+} are 3.502×10^{-10} cm² s⁻¹ for insertion and 6.238×10^{-11} cm² s⁻¹ for extraction in the Ni²⁺/Ni⁴⁺ redox couple region. The high Li⁺ mobility may be the root of the very different kinetic behaviors of Li⁺ transfer in the NCM material from previously reports.

4. Conclusion

In summary, the NCM material can conserve great structural reversibility even cycle up to 4.8 V, with absolutely suppression of H3 phase. The much smaller cell parameters variation and nearly zero change in unit cell volume provide a quality NCM sample for understanding its intrinsic electrochemical kinetics. With the combination of *in situ* synchrotron diffraction and electrochemical studies on thin and thick electrodes, we reveal that cluster scale conductivity relating to active particles population may be responsible for the 10% inert electrode material in thick electrode during cycling, which would result in capacity attenuation and polarization. CV characterizations of both thick and thin NCM electrodes in voltage region 2.0-5.0 V confirm the contribution of kinetic behaviors to electrochemical performances, reveal slightly kinetic difference between lithium insertion and extraction process, and suggest the use of a varying kinetic parameter is necessary for understanding the transport processes in NCM. Diffusive models based on CV curves clarify that the charge transfer in the as-prepared NCM is not dominated by Li^+ solid state mass transport but close to behaving like in a thin-layer, where the lithiation/delithiation takes place in the entire bulk of the particles without concentration gradient. This study is expected to be useful in future work in the Li-Co-Mn-Ni-O pseudo-quaternary system for 5 V chemistry.

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Table captions

Table 1. Atomic Positions of NCM with refinement of Neutron data.

Table 2. The potentials of the redox peaks and the intervals ($\Delta V/V$) for the thick and thin NCM electrodes at a sweep rate of 0.1 mV s^{-1} .

Table 3. The b -value for both the cathodic and anodic peaks in in Equation (1).

Table 4. Lithium ion diffusion coefficient (D_{Li^+} , $\text{cm}^2 \text{ s}^{-1}$) of the NCM samples in regime-a and regime-b.

Table 1

Element	Site	x	y	z	Occupancy	100*Uiso
Li	3b	0	0	0	0.970(1)	0.876(65)
	3a	0	0	0.5	0.030(1)	
Ni	3b	0	0	0	0.030(1)	0.139
	3a	0	0	0.5	0.304(1)	
Co	3a	0	0	0.5	0.333	
Mn	3a	0	0	0.5	0.333	
O	6c	0	0	0.2410	1	0.647

Table 2

Electrode type		The Ni ²⁺ /Ni ⁴⁺ couple [V]			The Co ³⁺ /Co ⁴⁺ couple [V]		
		Anodic-1 st	Cathodic-1 st	ΔV	Anodic-2 nd	Cathodic-2 nd	ΔV
Thick	1 st scan	3.837	3.630	0.207	4.668	4.569	0.099
	2 nd scan	3.813	3.627	0.186	4.592	4.528	0.064
Thin	1 st scan	3.803	3.673	0.130	4.653	4.592	0.061
	2 nd scan	3.768	3.673	0.095	4.588	4.557	0.031
	3 rd scan	3.754	3.670	0.084	4.569	4.534	0.035
	4 th scan	3.761	3.670	0.091	4.562	4.515	0.047
	5 th scan	3.761	3.667	0.094	4.553	4.492	0.061

Table 3

	The Ni ²⁺ /Ni ⁴⁺ couple		The Co ³⁺ /Co ⁴⁺ couple	
	Anodic-1 st	Cathodic-1 st	Anodic-2 nd	Cathodic-2 nd
<i>b</i>	0.907	0.825	0.905	0.918

Table 4

	The Ni ²⁺ /Ni ⁴⁺ couple		The Co ³⁺ /Co ⁴⁺ couple	
	Anodic-1 st	Cathodic-1 st	Anodic-2 nd	Cathodic-2 nd
(a)	2.12×10 ⁻⁸	4.76×10 ⁻⁹	1.85×10 ⁻⁹	2.37×10 ⁻¹⁰
(b)	1.15×10 ⁻⁷	3.69×10 ⁻⁸	2.45×10 ⁻⁸	2.04×10 ⁻⁸

Stable dual-redox pairs and thin-layer like kinetics benefit NCM cathode for 5V lithium chemistry.

Figure captions

Figure 1. Results of Rietveld refinement to a) *ex situ* synchrotron pattern and b) ND pattern obtained for pristine NCM material assuming space group symmetry of. Black: Calculated intensities; Red: observed intensities; Blue: difference between observed and calculated intensities; Green: positions of Bragg reflections.

Figure 2. a) SEM images at different magnifications; b) EDS analyses; c) Particle size distributions of NCM.

Figure 3. a) Diffraction patterns obtained during electrochemical characterization of NCM active material; b) Comparison of first (pristine) and last (discharge to 2.8 V after two full electrochemical cycles) diffraction patterns to verify whether irreversible transitions have occurred during electrochemical cycling; c) Evolution of lattice parameters versus number of diffraction patterns as obtained from Rietveld refinement to *in situ* XRD measurements.

Figure 4. a) Small amounts of pristine NCM materials do not take part in electrochemical cycling. Especially those states of charge with largely changed lattice parameters clearly exhibit reflections stemming from an inactive phase (indicated by arrows). b) Exemplarily: Rietveld refinement to diffraction pattern Nr. 24. Black: Calculated intensities; red: observed intensities; blue: difference between observed and calculated intensities; green: positions of Bragg reflections.

Figure 5. a) The 1st cycle discharge capacity as a function of the electrode loading for NCM electrodes at 36 mA g⁻¹ in the voltage window of 2.8-4.8 V; b) First & second

charge/discharge profiles of NCM on the thin and thick NCM electrodes. Solid and dotted lines refer, respectively, to first and second cycles.

Figure 6. Cyclic voltammograms of NCM at various scan rates on thick electrode: a) 0.1 mV s^{-1} ; and thin electrodes: b) 0.1 mV s^{-1} , c) 0.5 mV s^{-1} , d) 1 mV s^{-1} for the first 5 cycles. The electrode loading in thick electrode is ca. 3.582 mg cm^{-2} , in thin electrode is in the range of $0.413\sim 0.527 \text{ mg cm}^{-2}$, respectively.

Figure 7. Corrected cathodic and anodic peak currents $\log(I_p/A)$ are plotted versus $\log(v/V \text{ s}^{-1})$ with v from 0.02 to 5 mV s^{-1} .

Figure 8. Peak current I_p/A as a function of the square root of scan rate $(v/V \text{ s}^{-1})^{1/2}$ in the charge and discharge regions for the NCM sample with the scan rates ranging from 0.02 to 5 mV s^{-1} .

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8