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**$\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ CATHODE MATERIALS FOR
LITHIUM (-ION) BATTERIES**

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ENERGY RESEARCH INSTITUTE @ NTU (ERI@N)**

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LITHIUM (-ION) BATTERIES**

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A thesis submitted to the Nanyang Technological
University in partial fulfilment of the requirement for
the degree of
Doctor of Philosophy

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Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

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Date

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Student Name

Abstract

The current state-of-the-art lithium ion batteries (LIBs) have dominated the small format battery market for portable electronic devices, *i.e.*, 3C products, namely, computer, communication and consumer electronics. The implementation of such technologies into automotive like hybrid (HEVs), plug-in (PHEVs), or fully battery electric vehicles (BEVs) is also quite successful. However, the realization of pure electrical propulsion requires battery materials that enable high energies to meet demands of a ~ 500 km driving range, and a 10-year lifetime with driving range of 250,000 km. To achieve such a goal, the key challenge for both chemists and electrochemical engineers lies in increasing the battery energy density, while retains a long cycle life. At the moment, cathode materials remain the bottleneck due to their rather low capacity, compared with anode materials (generally graphite). Among all the common cathode materials, layered $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ (NCM) has overwhelming advantages for its high reversible capacity, rather low cost, good environmental benignity and high structural stability. However, the current NCM still suffers from two notable shortcomings: 1) poor rate capability especially at high C-rates due to rather sluggish Li^+ diffusion kinetics; 2) fatal capacity degradation upon prolonged cycles mainly resulting from side reactions between electrode and electrolyte. Therefore, further improvements are highly desired to address these issues and satisfy the requirements for practical applications.

Bearing these targets in mind, the main aims of my Ph.D. project are: 1) synthesis of NCM cathode materials with high C-rate capability and stable long-term cyclability; 2) demonstration of their practical feasibility in full cell applications, both by fabricating full lithium-ion cells with a combination of our modified cathode electrode, and via directly employing metallic lithium as anode electrode to assemble lithium metal cells (in ionic liquid electrolyte system).

To address the issue of poor C-rate capability, we employed a strategy of preparation of 1D bar-like $\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$ with preferentially exposed

{010} electrochemically active facets, which provide more open structure for unimpeded Li^+ migration. In addition, the diffusion pathways of lithium ions are greatly reduced because of the bar shape. All these factors together contribute to the achievement of significantly enhanced lithium ion diffusivity, and thus superior high C-rate capability.

Aiming at addressing the strong capacity fading issue, we adopted a surface coating strategy to stabilize the electrode/electrolyte interface and prevent detrimental side reactions. The amorphous MnPO_4 coating layer acts as an ideal protective layer via physically isolating the contact between NCM active material and electrolyte. Additionally, the MnPO_4 coating enhances the lithium de-/intercalation kinetics in terms of the apparent lithium ion diffusion coefficient. As a result, MP-NCM-based electrodes achieve greatly enhanced C rate capability and superior cycling stability – even under exertive conditions like extended operational potential windows, elevated temperature, and higher active material mass loadings. Through a combination of MP-NCM and commercial graphite, we further fabricated graphite/MP-NCM full lithium-ion batteries, which show remarkable long-term cycling stability (capacity retention ratio up to 74.1% over 2000 cycles at 1C), and deliver a high gravimetric energy density of 376.2 Wh kg^{-1} , demonstrating great practical feasibility. Employing an intrinsically safer electrolyte system, *ca.*, ionic liquid as alternative, the as-fabricated lithium metal batteries allow for outstanding cycling stabilities with a capacity retention of well above 85% after 2000 cycles.

Currently, the commercial electrode fabrication generally employs a large portion of toxic components and processing solvents (*i.e.*, NMP), particularly for cathode electrodes. To design greener LIBs, in this thesis, we also dedicated to replacing the conventional organic PVDF-based binder with aqueous CMC-based binder and investigating its effects in electrochemical performance.

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Figure 8.9 *In situ* HT-XRD diffractograms recorded for electrodes based on (a) NCM and (b) MP-NCM in their charged state (4.3 V).

Figure 8.10 XRD diffractograms of (a) the heating stage together with graphite dome and (b) the heating stage only.

Figure 8.11 Contour plots the evolution of the (003) and (104) reflections upon heating from 30 to 600 °C for charged (4.3 V) electrodes based on (a) NCM and (b) MP-NCM.

Figure 8.12 DSC profiles of charged electrodes (4.3 V) based on NCM (in black) and MP-NCM (in red) as active material.

Figure 8.13 (a) and (b) TEM images of MP-NCM electrode after 100 cycles at 0.1 C.

Abbreviations

ALD	Atomic Layer Deposition
BET	Brunauer-Emmett-Teller
BEV	Battery Electric Vehicle
ca.	<i>Circa</i>
CB	Carbon Black
CE	Coulombic Efficiency
CEI	Cathode Electrolyte Interface
CV	Cyclic Voltammetry
CMC	Carboxymethyl Cellulose
DEC	Diethyl Carbonate
DIW	Deionized Water
DMC	Dimethyl Carbonate
DSC	Differential Scanning Calorimetry
EC	Ethylene Carbonate
EDS	Energy Dispersive X-ray Spectroscopy
EIS	Electrochemical Impedance Spectroscopy
EMC	Ethyl-Methyl Carbonate
EoL	End-of-Life
EPS	Ethoxy-Functional Polysiloxane
ESW	Electrochemical Stability Window
etc.	<i>et cetera</i>
EVs	Electric Vehicles
FESEM	Field-Emission Scanning Electron Microscopy
FIB	Focused Ion Beam
GITT	Galvanostatic Intermittent Titration
HEV	Hybrid Electric Vehicle
HOMO	Highest Occupied Molecular Orbital
HRTEM	High Resolution Transmission Electron Microscopy
ICP-AES	Inductively Coupled Plasma-Atomic Emission

Spectrometry

i.e.	<i>id est</i>
LCO	Lithium Cobalt Oxide
LCSU	Local Coordination Structure Unit
LIBs	Lithium-Ion Batteries
LMO	Lithium Manganese Oxide
LNO	Lithium Nickel Oxide
LUMO	Lowest Unoccupied Molecular Orbital
MOF	Metal Organic Frameworks
MPCVD	Microwave Plasma Chemical Vapor Deposition
NCM	Lithium Nickel Cobalt Manganese Oxide
NMP	N-Methyl-2-Pyrrolidone
OCV	Open Circuit Voltage
ODH	Oxygen Dumbbell Hop
PEDOT	Poly(3,4-ethylenedioxy-thiophene)
PEG	Poly(ethylene glycol)
PEO	Poly(ethylene oxide)
PHEV	Plug-in Hybrid Electric Vehicle
PI	Polyamide
PITT	Potentiostatic Intermittent Titration
PPy	polypyrrole
PVB	Polyvinylbutyral
PVdF	Polyvinylidene-di-Fluoride
rGO	Reduced Graphene Oxide
SEI	Solid Electrolyte Interface
SEM	Scanning Electron Microscopy
SHE	Standard Hydrogen Electrode
TSH	Tetrahedral Site Hop
TEM	Transmission Electron Microscopy
TEOS	Tetraethyl Orthosilicate

Abbreviations

TGA	Thermalgravimetric Analysis	
VC	Vinylene Carbonate	
vs.	<i>versus</i>	
XPS	X-ray Photoelectron Spectroscopy	
XRD	X-ray Diffraction	
X-ray diffraction and mass spectroscopy		TR-XRD/MS

Chapter 1

Introduction

In this chapter, we firstly present a brief introduction about background, hypothesis/problem statement based on the current main challenges and bottlenecks. Then we propose our objectives and scope of the Ph.D project. A dissertation overview which briefly describes each chapter is also included in this chapter. Finally, the findings and outcomes of the thesis works are also provided.

1.1 Background

The current energy economy based on fossil fuels is facing big challenges due to a series of factors, ranging from a continuously increased demand for oil, to the consumption of non-renewable resources (*ca.*, coal), and to national vulnerabilities that endanger social/country stability [1]. In addition, the ever-growing consumption of fossil fuels has caused serious CO₂ emissions. Evidenced by a dramatic jump during the last three decades, the level of CO₂ emission has almost doubled passing from 1980 to 2016. It not only pollutes the air but also leads to incremental global temperature concomitantly with dramatic climate changes through the well-known “greenhouse effect” [1, 2]. Although the global energy-related CO₂ emissions show a flat from 2014 to 2016 (Figure 1.1) according to the International Energy Agency, however, it is too soon to jump to a conclusion that global emissions have definitely peaked. Forced by these global concerns, more attentions tend to be paid on national effort to not only reevaluate the use of alternative sustainable energy sources but also to shift the internal combustion engines of moving ground transportation towards electrical propulsion with ideally, zero emission vehicles, such as electric vehicles (EVs) [3, 4].

Figure 1.1 Global CO₂ emissions (modified from online sources).

In recent years, although we have evidenced a quite impressive progress in the development of technology for harvesting sustainable energies, including but not limited to wave power, wind energy, tidal power, solar energy, bioenergy, geothermal energy, hydroelectricity. However, these sustainable energy sources generally fluctuate in time and variate in locations. Hence, the use of such sustainable energies for electricity production requires the availability of suitable energy storage technologies. Battery emerges as the most convenient technique for energy storage because it stores electrochemical energy which is later delivered in form of electrical energy [4].

Figure 1.2 Specific power versus energy densities of various secondary batteries [5].

The development of batteries could be traced back to 1798 when Alessandro Volta firstly invented the “VOLTA pile” using zinc and silver plates, connected by paper soaked in brine [6]. Primary lithium batteries became a commercial reality during the 1970s. Secondary batteries, also known as rechargeable batteries, have evolved from lead-acid (PbAc), through nickel-cadmium batteries (Ni-Cd), alkaline zinc-manganese dioxide (Zn-MnO_2) and nickel-metal hydride (Ni-MH) to lithium ion batteries (LIBs) over the years [7]. The latter outperforms, by at least a factor of 2.5 [5], in case of delivered energy

without sacrificing high specific power (Figure 1.2). LIBs emerged as a promising alternative for the formers, owing to the overwhelming advantages of high specific capacity benefiting from its low molecular weight [8], fast Li^+ diffusion kinetics on account of its small ionic radius, and high output voltages which further lead to high energy densities owing to its low redox potential [$E^\circ(\text{Li}^+/\text{Li}) = -3.04 \text{ V}$ vs. standard hydrogen electrode (SHE)] [9, 10].

Figure 1.3 Development of specific energy and energy density of LIBs (cell level) between year 1991 and 2017, following their commercialization by Sony in 1991. Values are based on the standard cylindrical 18650 lithium ion cell and are taken from cell producers' data sheet [11].

Murphy et al. firstly introduced the concept [12], soon, the well-known Li-ion or rocking-chair technology [8] was realized by Scrosati et al. [13] in late 1980s and early 1990s. The latest technological leap in LIB field occurred in 1991 owing to the market entry of the first commercial LIB by SONY Corporation with a high gravimetric energy of 80 Wh kg^{-1} and a volumetric energy of 200 Wh L^{-1} and a voltage of $\approx 3.7 \text{ V}$ [11, 14]. Figure 1.3 shows the evolution of LIBs regarding gravimetric and volumetric energy density, spanning from 1991 to 2017. So far, the development of gravimetric and volumetric energy densities has increased more than three folds, *ca.*, from 80 to

256 Wh kg⁻¹, from 200 to 697 Wh L⁻¹, respectively [11]. This incremental performance is driven not only by technical achievements, but also by various demands from consumers and society such as rising application requirements as well as a growing trend for sustainability and lower costs. The current state-of-the-art LIBs not only have dominated the small format battery market for portable electronic devices (3 C products, namely, computer, communication and consumer electronics) [15, 16], but also have been successfully implemented for auto motives like hybrid (HEVs), plug-in (PHEVs), or fully battery electric vehicles (BEVs) as well as for stationary energy storage [11]. Figure 1.4 displays the predicted market drastic expansion of LIBs by a factor of 10 in US dollar (USD), ranging from 2010 to 2020, by LG Economic Research Institute [17].

Figure 1.4 Predicted market of secondary batteries by LG Economic Research Institute [17].

1.2 Hypothesis/Problem Statement

At the moment, the total driving range of commercial BEV is approximately 150 – 200 km, *ca.*, 172 km for NISSAN LEAF and 183 km for BMW I3 [18]. Although great achievements have been made, the realization of pure electrical propulsion requires battery materials that enable high energies to meet demands of a ~500 km driving range from consumers [19, 20], and a 10 years lifetime with driving range of 150,000 miles [17]. To achieve such a goal, the key challenge for both chemists and electrochemical engineers lies in increasing the battery energy densities, and meanwhile to retain a long cycling life with a reasonable rate operated in safe conditions [21]. The energy density is calculated by electrodes' specific capacity and cell's working voltage (see Eq. 1.1), the latter can be expressed as the differential potential of cathode (μ_C) and anode (μ_A) (see Eq. 1.2).

$$Energy = \int_0^Q V(q) dq = \int_0^t IV(t) dt \quad \text{Eq. 1.1}$$

$$V = \frac{(\mu)_A - (\mu)_C}{e} \quad \text{Eq. 1.2}$$

Therefore, two research directions are naturally formed, one aims at seeking for cathode materials with higher specific capacity, the other focuses on searching for cathode materials with high operation voltage. The differential voltage is controlled either by the electrochemical stability window (ESW) of electrolyte or by the top of the anion-p bands of cathodes (O-2p bands for transition metal oxide cathodes) [10, 21]. Generally, the μ_C of cathode should be located above the highest occupied molecular orbitals (HOMO) of electrolyte, while, the μ_A of anode should be below the lowest unoccupied molecular orbitals (LUMO) as depicted in Figure 1.5a. Otherwise, a μ_A located above the electrolyte LUMO would reduce the electrolyte, and a μ_C located below the HOMO would oxidize the electrolyte except for the block of electrode electrolyte reactions via forming a passivation layer (SEI). Taking LiCoO_2 for example (Figure 1.5b), if the anion p-band peak exceeds the energy state of transition metal ions (*e.g.*, $\text{Co}^{3+}/\text{Co}^{4+}$), the anion O^{2-} would be oxidized with the formation of gaseous O_2 , causing series of issues that will be discussed in detail later (Chapter 2). Considering of the conventional organic liquid electrolyte [1M of LiPF_6

dissolved in ethyl carbonate-dimethyl carbonate (EC–DMC, v:v = 1:1)], the practical HOMO is located at 4.3 eV below μ_{Li} . The investigation of high-voltage cathodes, such as spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (4.70–4.75 V) and olivine LiMnPO_4 (4.1 V), LiCoPO_4 (4.8 V), LiNiPO_4 (5.2 V), needs new electrolyte that can operate normally at such high voltages.

Figure 1.5 (a) Relative energies of electrolyte window and the relationship between electrochemical potentials of electrodes and electrolyte. (b) A scheme of energy electrochemical potentials of metallic Li and LiCoO_2 , and their relative energy positions with respect to the HOMO and LUMO of electrolyte.

The exploration of cathode materials with high capacity can also be divided into two directions, *ca.*, lithium and manganese-rich NCM [$x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$, denoted as LMR-NCM] and Ni-based NCM ($\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$, hereafter denoted as NCM_{xyz}). While LMR-NCM with layered structure can deliver high specific capacity (*ca.*, 250 mAh g^{-1} at 0.1C

rate), these materials face some intrinsic challenges, such as: 1) unavoidable voltage decay due to the continuous irreversible phase transition from layered to spinel structure [22-24]; 2) release of oxygen because of the activation of Li_2MnO_3 over 4.5 V during the initial delithiation process, posing a serious safety issue [25]; and 3) electrolyte decomposition because of the wide working voltage range (generally 2.5–4.8 V). These features give rise to eventual severe capacity degradation, energy density decay and poor rate capability, making the commercialization of such a cathode more difficult [26]. On the other hand, nickel-based NCMs have recently attracted enormous attention as they exhibit higher capacity and lower cost as compared to the commercial NCM_{333} , as a result of the increased fraction of the electrochemically active element (Ni). However, as common issues for NCM, the poor rate capability as well as strong capacity fading upon long-term cycling still need to be addressed. Because of the similar radii of Ni^{2+} (0.69 Å) and Li^+ (0.76 Å), the cation mixing tends to be more severe at higher nickel content. Particularly, the Ni-rich NCM (Ni content > 0.5) has, according to some reports [27, 28], resulted into more severe capacity deterioration due to thermal and structural instabilities. The detrimental side reactions between electrode and electrolyte deteriorate the cell performance and even cause some safety issues. Generally, the Ni-rich NCM has strong tendency to release oxygen at fully charged state because the Ni^{4+} are reduced to Ni^{2+} , which would oxidize the electrolyte and cause severe electrolyte decomposition. Consequently, some serious safety issues, such as thermal runaway, exhibiting sparks, fires and even explosion could be triggered [29, 30]. What's more, the loss of oxygen from surface of NCM will lead to weaker bonding interaction with transition metal atoms, leading to the migration of transition metal ions into lithium slabs. Even worse, the transition metal dissolution into organic electrolyte will occur in acidic electrolyte (HF attack) [31, 32]. The rearranged structure near the surface of layered ($R(-)3m$) cathode material can easily trigger the structural transformation, forming disordered spinel phase ($Fd(-)3m$) and finally rock salt phase ($Fm(-)3m$) [33-

35]. Especially, the structural transformation aggravates at higher temperature (> 55 °C) and higher operating voltage (~4.6 V) [36, 37]. According to Hwang *et al.* [38], the poor thermodynamic feature at elevated temperature is ascribed to the easier reduction from Ni^{4+} to Ni^{2+} , in conjunction with severe oxygen loss. Through time-resolved X-ray diffraction & mass spectrometry (TR-XRD/MS), Bak *et al.* [39] revealed the same phase transformation upon heating the charged electrode. Taken together, the deterioration of chemical and structural stability of cathode material will be accelerated, leading to continuous capacity decay and thus inferior electrochemical performances [40, 41].

1.3 Objectives and Scope

Therefore, my Ph.D project targets are:

- 1) *Synthesis of Ni-rich and Co-poor NCM_{424} with high C-rate capability and stable long-term cycling performance.*
- 2) *Further surface modification of NCM_{424} via coating a conformal and uniform layer of amorphous manganese phosphate to suppress detrimental side reactions at electrode/electrolyte interface, and hence lead to enhanced C-rate capability and long-term cycling performance, even under some exertive conditions.*
- 3) *Full lithium-ion cell fabrication incorporating with surface modified NCM and commercial graphite to demonstrate our commercialization potential; full lithium metal cell fabrication with a combination of surface modified NCM and metallic lithium in an intrinsically safer ionic liquid system.*
- 4) *Applications of NCM toward greener lithium ion batteries by substituting organic PVdF-based binder with aqueous CMC-based binder.*
- 5) *Extension of the surface coating strategy to Ni-rich NCM, i.e., NCM_{622} , to pursue higher capacity and thus higher energy density, in pace with the current research interest of both industries and academia.*

1.4 Dissertation Overview

Chapter 1 provides an overall introduction about the whole thesis, including the background and motivation, and the objectives and scopes are then outlined.

Chapter 2 reviews the literature concerning the development of layered cathode materials, including LiCoO_2 , LiNiO_2 , LiMnO_2 and $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$. A summarization of commonly used synthesis methods for $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ is also provided. In addition, an overview about recent progress in surface modification of $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ is presented.

Chapter 3 provides all the experimental methodologies including sample synthesis, electrode preparation, and cell fabrication *etc.*, lists and discusses all the material characterization techniques as well as their working principles involved within this thesis.

Chapter 4 demonstrates the synthesis of 1D bar-like NCM_{424} with superior long-term capacity retention and high rate capability that are attributed to: 1) the synthesis design strategy leading to 1D bars with preferentially exposed $\{010\}$ electrochemical active facets, which provide more open structure for unimpeded Li^+ migration; 2) the greatly reduced diffusion pathway of lithium ions benefiting from the bar shape morphology.

Chapter 5 illustrates the design and synthesis of MnPO_4 -coated NCM_{424} with outstanding cycling stability and enhanced de-/lithiation kinetics for lithium batteries. The coating layer of MnPO_4 acts as an ideal protective layer to physically isolate NCM active material and electrolyte. Thus, a successfully stabilized electrode/electrolyte interface could be achieved as a result of suppressed detrimental side reactions. Additionally, the MnPO_4 coating enhances the lithium de-/intercalation kinetics in terms of the apparent lithium ion diffusion coefficient.

Chapter 6 presents a long-life graphite/ $\text{MnPO}_4@\text{NCM}_{424}$ full lithium-ion cell with high energy/power densities, demonstrating strong potential for commercialization, and $\text{Li}/\text{MnPO}_4@\text{NCM}_{424}$ full lithium metal cell with outstanding long cycling lifetime in ionic liquid electrolyte system.

Chapter 7 provides a greener application via substituting conventional organic

PVDF-based binder with aqueous CMC-based binder for LIBs and investigates the binder effect on cell electrochemical performances.

Chapter 8 draws a conclusion of the whole thesis work and gives some recommended future works at the end of this chapter.

Chapter 2

Literature Review

This chapter starts with an explanation of the working mechanism of LIBs, presents some basic definitions of batteries, summarizes the development of layered cathode materials, including LiCoO_2 , LiNiO_2 , LiMnO_2 and $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ series. The most commonly-used synthesis routes of $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ are also summarized in this chapter. We also give an overview about the recent progress in $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ surface modifications.

2.1 Working Mechanism of LIBs

Figure 2.1 demonstrates the basic working mechanism of LIBs. A typical lithium ion battery system generally includes three main components, *ca.*, cathode, anode, and electrolyte. In the current state-of-the-art LIB system, cathode and anode materials are both intercalation compounds. Generally, cathode materials are transition metal compounds, including spinel compounds with one-dimensional diffusion pathways (*i.e.*, LiMn_2O_4), layered compounds with two-dimensional diffusion pathways (*i.e.*, LiCoO_2 , $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$, $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$), and olivine compounds with three-dimensional pathways (*i.e.*, LiFePO_4). As for anode side, graphite is globally deemed as the most commonly used material. The lithium ion battery system is assembled at “discharged” state, therefore, the operation of LIBs always starts with a charging step. During charging step, the lithium ions will extract from cathode host material, migrate through electrolyte, and then insert into anode material. Lithium ions’ de-intercalation results in a change in the charge distribution inside the cathode host material skeleton, and thus an overall change in the material charge [42]. This, in turn, causes concurrently electron move from cathode side to anode side through the external circuit. Upon battery charging, the electric energy is stored as electrochemical energy [43]. The discharging process simply reverses the process of charging step, *i.e.*, the electrochemical energy is transferred into electric energy. Overall, the operation of LIBs follows the reaction equations shown below:

The LIBs can cycle a long lifetime via the reversible the “rocking” of lithium ions between cathode and anode materials.

Figure 2.1 Schematic of a LIB [5].

2.2 Battery Definitions

(a) *Theoretical specific capacity (Q_{th})*

$$Q_{th} = \frac{n \times F}{3.6 \times M_w} \quad \text{Eq. 2.4}$$

The theoretical specific capacity, which is usually expressed in mAh g^{-1} , Ah kg^{-1} , can be calculated based on Faraday's Law (Eq. 2.4), where n is electron numbers exchanged per mol, M_w (Kg mol^{-1}) is molar weight of active material, F is Faraday constant (96485 C mol^{-1} , $96485 \text{ s A mol}^{-1}$). The constant value 3.6 is derived by the normalization of $1 \text{ Ah} = 3600 \text{ As} = 3600 \text{ C}$.

(b) *Practical capacity (Q)*

$$Q = \int_0^t I dt = \int_0^Q dq \quad \text{Eq. 2.5}$$

The practical capacity can be calculated based on Eq. 2.5, where I (A) is current, t (h) is time and q is charge. The practical capacity, which can also be expressed in mAh g^{-1} , Ah kg^{-1} , depends on the current applied upon testing.

(c) *Energy*

$$\text{energy} = \int_0^t IV(t) dt = \int_0^t P(t) dt = \int_0^Q V(q) dq \quad \text{Eq. 2.6}$$

The energy can be calculated based on Eq. 2.6, where I (A) is current, t (h) is

time, P (W) is power, V (V) is voltage. The energy is often expressed in $Wh\ kg^{-1}$ (gravimetric energy) or $Wh\ L^{-1}$ (volumetric energy).

(d) *Coulombic efficiency (η)*

$$\eta = \frac{Q_{discharge}}{Q_{charge}} \times 100\% \quad \text{Eq. 2.7}$$

The Coulombic efficiency (expressed in %) is generally used to evaluate the reversibility of charge and discharge processes and it can be obtained from Eq. 2.7.

(e) *Capacity retention ratio*

$$\text{Capacity retention ratio} = \frac{Q_n}{Q_1} \times 100\% \quad \text{Eq. 2.8}$$

The capacity retention ratio (Eq. 2.8) is defined by the ratio of discharge capacity of n^{th} cycle (Q_n) and 1st cycle (Q_1).

(f) *C rate*

The definition of C rate is the current applied to fully dis-/charged the active material within a fixed amount of time (generally expressed in hour). For instance, 1C refers to the current necessary to fully dis-/charge the active material in one hour.

(g) *End-of-Life (EoL)*

End-of-life criteria is defined as the cycling numbers of batteries that enable reversible dis-/charge with a capacity retention ratio maintained above 80%.

2.3 Development of Layered Cathode Materials

2.3.1 $LiCoO_2$

In 1980, Goodenough *et al.* [44] firstly synthesized $LiCoO_2$ (LCO). With the success of cell commercialization by SONY in early 1990s [42, 45], LCO becomes the most widely used cathode materials and dominates the market of portable electronic devices. The ideal LCO has α - $NaFeO_2$ layered structure with overall hexagonal symmetry (space group, $R(-3)m$, number 166) [46]. CoO_2 slabs alternate with lithium layers along c axis. The oxygen anions form a close-packed fcc lattice and cations (Co, Li) occupy the six-coordinated

octahedral crystal sites [43]. Although LCO exhibits quite high theoretical capacity, *i.e.*, 274 mAh g⁻¹, however, the practical reversible capacity is limited to ~ 140 mAh g⁻¹. It is believed that LCO can only operate reversibly on the condition of $x < 0.5$ (Li_{1-x}CoO₂, charge up to maximum 4.2 V, *vs.* Li/Li⁺) to avoid severe structural destruction [47]. Additionally, cobalt had pushed researches to search for other alternatives due to its drawbacks of high cost and toxicity.

2.3.2 LiNiO₂

The worldwide distribution of Nickel source is richer than cobalt, therefore naturally people would consider it as a cheaper alternative. In fact, the research of LiNiO₂ (LNO) could be tracked back to 1954 by Dyer *et al.* [48]. However, the intensive studies of LNO only started in the 1990s by Dahn *et al.* with the advent of successful implement of LCO [19, 49, 50]. Nevertheless, the synthesis of stoichiometric LNO is very difficult on account of lower thermodynamic stability with respect to LCO, as well as the migration of nickel into lithium layers [14, 51]. The latter may even cause the formation of electrochemical inactive *Fm(-)3m* phase once the occupation of nickel exceeds certain amount [19]. LNO also suffers from strong tendency of reaction with CO₂, H₂O from air atmosphere, forming electrochemical inactive Li₂CO₃ and LiOH [50]. When incorporating with aqueous-based binder in the slurry preparation process, the high PH values of Li₂CO₃ and LiOH would corrode aluminum current collector severely, concomitantly with the formation of water soluble Al species (*i.e.*, Al(OH)₄⁻, AlO₂⁻) [52]. Another serious problem of LNO is the structural transformation to monoclinic phase (LiNi_xO₂, 0.5 < x < 0.75) [53] and another hexagonal phase (LiNi_xO₂, x < 0.4) [54]. All these, together, lead to poor electrochemical performance.

2.3.3 LiMnO₂

Given the economy efficiency and environmental friendliness, the

isostructural LiMnO_2 (LMO) is even better alternative compared to LNO. However, Mn^{3+} is *Jahn-Teller* active, thus the layered phase would gradually change to spinel phase, causing strong capacity loss upon cycling. The difficulty in synthesizing pure LMO phase also aroused some concerns due to the occurrence of orthorhombic phase ($Pmmn$), which is more thermally stable. Nevertheless, this phase exhibits quite poor electrochemical active property [14, 55, 56].

2.3.4 $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$

Since pure LMO ($M = \text{Ni}, \text{Co}, \text{Mn}$) could not get satisfactory electrochemical performance, researchers found that doping can efficiently enhance the cell performance. With a successful trial in binary cathodes $\text{LiNi}_{1-x}\text{Mn}_x\text{O}_2$ which was initially introduced by Rossen *et al.* [57], layered ternary solid solution, *ca.*, $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$ ($0 \leq x \leq 0.5$, $0 \leq y \leq 0.3$), was firstly synthesized by Liu *et al.* [58] in 1999. Two years later, Ohzuku *et al.* prepared NCM_{333} , which could be deemed as a solid solution of LiNiO_2 , LiCoO_2 and LiMnO_2 with a ratio of 1:1:1. The NCM_{333} delivered a reversible capacity of $\sim 150 \text{ mAh g}^{-1}$ (charged up to 4.2 V) and $\sim 220 \text{ mAh g}^{-1}$ (charged up to 5 V), respectively. Through a combined computational and XANES study of NCM_{333} by Ceder's group [59], it was revealed that nickel is divalent, cobalt is trivalent while manganese is tetravalent in the pristine material, respectively. The main contribution of capacity comes from nickel via a two-electron redox reaction, *ca.*, $\text{Ni}^{2+}/\text{Ni}^{3+}$ and $\text{Ni}^{3+}/\text{Ni}^{4+}$, corresponding to lithium content (x) of $2/3 \leq x \leq 1$ and $1/3 \leq x \leq 2/3$, respectively. When lithium content $0 \leq x \leq 1/3$, the redox reaction of $\text{Co}^{3+}/\text{Co}^{4+}$ contributes to the capacity. In the NCM system, each element, *ca.*, nickel, cobalt and manganese plays different functions. For instance, as the main electrochemically active species, the majority capacity comes from the redox reactions of Ni ions (Ni^{2+} , Ni^{3+}) [60]. Co^{3+} ions are kept at trivalent states before all Ni ions oxidize to Ni^{4+} upon delithiation. Due to the high conductivity, the main roles of cobalt are to enhance the rate performance

and meanwhile suppress the cation mixing of $\text{Li}^+/\text{Ni}^{2+}$ [14, 61, 62]. Unlike the nickel and cobalt ions, the electrochemically inactive Mn^{4+} ions are beneficial for retaining the structural stability of NCM [61]. Similar to LCO, NCM exhibits the same well defined $\alpha\text{-NaFeO}_2$ layered structure with hexagonal crystalline (space group $R(-)3m$), where lithium ions occupy the $3b$ sites, transition metal cations M (M = Ni, Co, Mn) occupy the $3a$ sites, and O^{2-} anions occupy the $6c$ sites [62]. Three MO_2 slabs stack along c axis, forming the “O3” phase. Ideally, this layered structure can also be deemed as an ordered rock-salt structure, in which the lithium oxide and transition metal oxide slabs alternate along the $[111]$ direction [63]. However, due to similar radius of Li^+ and Ni^{2+} (0.76 Å vs. 0.69 Å), the inevitable cation mixing of $\text{Li}^+/\text{Ni}^{2+}$ lead to a “disordered rock-salt” structure [64]. The disordered material has a tendency to form the electrochemical inactive $Fm(-)3m$ phase once sufficient nickel ions occupy the lithium slabs, which appears as the same issue existing in pure LiNiO_2 . Fortunately, there’s a relatively easy way to qualitatively determine the degree of disorder via XRD analysis, *ca.*, the intensity ratio of (003) peak and (104) peak ($I_{(003)}/I_{(104)}$). The (003) peak disappears in the $Fm(-)3m$ phase, therefore, a higher $I_{(003)}/I_{(104)}$ ratio reveals less disorder [19]. It is generally believed that a ratio of $I_{(003)}/I_{(104)}$ over 1.2 indicates a desirable cation mixing [65]. The splitting of doublets (006)/(102) and (108)/(110) suggests a good hexagonal ordering of layered structure [28]. According to Dahn *et al.* [50], a lower ratio of $(I_{(006)}+I_{(102)})/I_{(101)}$ is also an indication of better hexagonal ordering.

Figure 2.2 Lithium ion diffusion mechanisms: (a) Oxygen dumbbell hop (ODH); (b) Tetrahedral site hop (TSH). Two lithium ions' migration pathways looking down on the Li_xCoO_2 crystal structure perpendicular to ab planes. The triangular grid are the lithium sites, the solid circles are Li^+ , the big empty circles are O^{2-} in the plane directly above the lithium plane, whereas the small empty circles are O^{2-} directly below the lithium plane. $\square$ correspond to lithium vacancies [66].

As mentioned earlier, NCM has two-dimensional diffusion pathways along ab plane, perpendicular to c axis. Ven and Ceder [66] adopted first-principles calculations to study the diffusion of lithium ions. It mainly follows two mechanisms, relying on the Li vacancy environment surrounding the hopping ion (Figure 2.2). The first mechanism is called oxygen dumbbell hop (ODH), in which the lithium ions diffuse through squeezing past a dumbbell of oxygen ions as shown in Figure 2.2a. The second mechanism is the so-called tetrahedral site hop (TSH), which involves the scenario of divacancy or a cluster with more than two vacancies. In case of TSH, the lithium ions diffuse via the tetrahedral site which is located in the center of two vacancies and initial hopping site (Figure 2.2b). It is worth noting that the activation energy barrier of TSH is always substantially lower than that of ODH. However, given the fact that TSH only occurs with a presence of divacancies, thus, the possibility of TSH at low delithiation is very low. Wei *et al.* [60] proposed a global view of lithium ion diffusion kinetics as a function of delithiation process ($\text{Li}_{1-x}\text{MO}_2$, $0 < x < 0.6$), as depicted in Figure 2.3. When delithiation starts, the Li slab space increases to facilitate faster Li diffusion benefiting from the broken of $\text{O}^{2-}-\text{Li}^+-\text{O}^{2-}$ bonds along the LiO_6 slabs, and thus to reduce effective diffusion barriers (E_{eff}) as well as the increased diffusion coefficient (D_s) [67]. Along with the processing of delithiation, the Ni^{2+} would be oxidized to Ni^{3+} and to Ni^{4+} , at the same time, the activation energy of both ODH and TSH increased. With the further delithiation, this effect would be dominant and thus cause increased E_{eff} and decreased D_s . With more divacancies or clusters occurs, TSH arises when $x > 1/6$ and dominates the hopping mechanism when the x approaches $1/3$. Consequently, the decreased E_{eff} ($E_{\text{eff}}^{\text{ODH}} > E_{\text{eff}}^{\text{TSH}}$) would outweigh the impact

of the increased activation energy caused by Ni oxidation. This gives rise to the increasing of D_s when the SOC surpasses the minimum D_s value ($x = 0.22 - 0.25$). Once the TSH dominates, the increase of D_s with a slower rate is a compromise between the competition of increased Li slab space and increased Ni valence state upon delithiation.

Figure 2.3 Kinetics tuning of Li-diffusion in a delithiation process [60].

With the ever-increasing desire for higher capacity, the pursue of higher content of nickel is quite necessary. This leads to a wide investigation of nickel based $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ (NCM_{xyz}) series, such as NCM_{424} , NCM_{433} , NCM_{525} , NCM_{523} , NCM_{532} , NCM_{622} , NCM_{715715} , NCM_{811} etc (Figure 2.4). In order to keep the total charge at neutral status, partial of Ni^{3+} ions are pushed to Ni^{2+} , in case of $x \neq z$. For instance, the $\text{Ni}^{2+}/\text{Ni}^{3+}$ ratios are 3:1 (NCM_{433}), 3:2 (NCM_{523}), 2:3 (NCM_{532}), 1:2 (NCM_{622}), 3:11 (NCM_{71515}) and 1:7 (NCM_{811}), respectively [60]. While, on the other hand, pure Ni^{2+} ions only exist when $x = z$ in $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ series, *i.e.*, NCM_{333} , NCM_{424} and NCM_{525} .

Figure 2.4 Triangular phase diagram of $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ with various compositions located in this triangular phase diagram.

Although higher nickel content would contribute to higher capacity, it is well-known that this is at the cost of decreased thermal stability. Bak *et al.* [39] investigated the structural evolutions and thermal stability of $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ series, including NCM_{433} , NCM_{523} , NCM_{622} and NCM_{811} . Through a systematic study via *in-situ* time-resolved XRD and mass spectrometry (TR-XRD/MS), it is revealed that the charged NCM underwent a decreased trend toward increased nickel content in terms of thermal stability, but an increased trend toward higher cobalt and manganese contents. Higher nickel content leads to lower onset phase transition temperature, *ca.*, 245 °C (NCM_{433}), 235 °C (NCM_{523}), 185 °C (NCM_{622}) and 135 °C (NCM_{811}), as shown in Figure 2.5a. With increased heating temperature, the phase of charged materials experiences a serial of transitions due to thermal decomposition (Figures 2.5a and b), from layered (space group $R(-)3m$) to spinel (space group $Fd(-)3m$), and to rock-salt (space group $Fm(-)3m$) [39]. Especially for those NCM with higher nickel contents, the poor thermal stability jeopardizes the safety of batteries due to the oxygen release at highly charged status. As a result, the oxidation of organic

electrolyte would trigger severe thermal runaway and even cause catastrophic cell failure [68, 69]. Noh *et al.* [70] revealed that the thermal stability of NCM also depends on the valence state of Ni, the Mn and Co contents, the lithium content and the $\text{Ni}^{2+}/\text{Li}^+$ cation mixing [71]. Zheng *et al.* [71] carried out a systematic study and proposed a microscopic picture for tuning the thermal stability of NCM materials through considering of all above-mentioned factors. The thermal stability of NCM, based on both simulation and experimental results, is closely related to the most unstable oxygen, which could be defined by the oxygen local coordination structure unit (LCSU, TM (Ni, Co, Mn)₃–O–Li_{3-x'}, $x' = 0-3$). Upon charging, the instability of oxygen can be aggravated, resulting from a synergistic effect from both Li vacancies and Ni oxidations. With same lithium content, oxygens, which are coordinated with more nickel in the LCSU, are more unstable (especially for Ni ions at highly oxidized status). This is in consistent with previous claims that higher Ni content tends to accelerate onset thermal decomposition temperatures, releasing huge amounts of oxygen. The $\text{Ni}^{2+}/\text{Li}^+$ cation mixing could lower the thermal stability for those materials with same Ni and Mn contents. However, the nickel ions in the Li layer would form 180° Ni–O–Ni super exchange chains (Figure 2.6). For such a reason, it would benefit for “Ni-rich” group materials. The doping of Mn and Co can adjust the thermal stability through adjusting the initial Ni valence state, the oxygen local coordination environment, and the $\text{Ni}^{2+}/\text{Li}^+$ mixing.

Figure 2.5 (a) Mass spectroscopy profiles for the oxygen and the related phase transitions temperature region for NMC samples (lower panel); (b) Phase stability plot of the de-lithiated NMC cathode materials upon heating as a function of various Ni contents [39].

Figure 2.6 Schematic illustration in terms of tuning of thermal stability upon delithiation process [71]. Green: Li; red: O; silver: Ni; purple: Mn; and blue: Co.

2.4 Summarization of Synthesis Routes of $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$

There are many synthesis methods for NCM, including solid-state reaction, sol-gel method, coprecipitation, hydrothermal, spray drying, and microwave-hydrothermal method etc. The synthesis of NCM always involves a high temperature calcination step, which is either a direct calcination of precursor or a solid-state calcination of precursor with other starting materials (usually lithium source). The synthesis methods are generally defined by the synthesis of precursors. In some cases, two or more methods can be combined for certain synthesis purposes. In this part, we will give a brief introduction of each method together with a summarization of some typical works.

(a) solid-state reaction [72-75]

The synthesis of cathode materials via solid-state reaction is simple, facile, cheap and easy for large-scale production. However, it is difficult to obtain NCM particles with homogeneous particle size distribution, resulting in the poor performance of the materials. Besides, the solid-state reaction can easily

form impure phase and thus lead to unsatisfactory cell performance [76]. Tan *et al.* [72] synthesized NCM₃₃₃ (particle sizes: ~ 150-200 nm) by mixing NiO, Co₂O₃, MnO₂ and 3mol% excess Li₂CO₃ in an agate mortar for half an hour, followed by pre-heating at 500 °C and a subsequent calcination step at 900 °C for 12 h. Instead of metal oxides, Tan *et al.* [75] prepared NCM₄₂₄ using acetates of lithium, nickel, cobalt and manganese as starting materials, which were mixed and ground by a pestle and mortar. The mixture was then pre-heated at 400 °C for 12 h and calcinated at 950 °C for another 12 h.

(b) sol-gel [77-81]

Generally, the sol-gel method allows intimate mixing at atomic level. This allows the production of compositionally homogeneous materials with small particle size and high specific surface area (macro pores) at low synthesis temperature. The microscopically porous NCM₃₃₃, interconnected by single crystal nanoparticles was prepared by Huang *et al.* [78] via a modified sol-gel method and a stepwise heating/cooling process. Lee *et al.* synthesized NCM₆₂₂ through sol-gel method, in which citric acid works as chelating agent. However, the large surface area, in turn, could consume plenty of electrolyte in order to form stabilized SEI passivation layer and thus cause a low initial Coulombic efficiency. In addition, sol-gel method usually involves relatively complex synthesis process and high cost, which are not beneficial for industrial production.

(c) coprecipitation [82-91]

At present, the coprecipitation method is the most commonly used method. Generally, a typical coprecipitation method can yield carbonates, oxalates, and hydroxides precursors. It has many advantages, such as small granularity, large scale production and low synthesis temperature. However, coprecipitation generally requires careful control of PH value, temperature, mixing speed and atmosphere to obtain homogenous precipitants. Through careful control of PH, chelating agent amount, and stirring speed etc., Lee *et al.* [82] successfully synthesized uniformly distributed (Ni_{1/3}Co_{1/3}Mn_{1/3})(OH)₂. Then LiOH·H₂O was

added and well mixed for a subsequent solid-state calcination step to form final product of NCM₃₃₃. The average particle size of the as-obtained spherical NCM₃₃₃ is about 10 μm with narrow particle size distribution, yielding a high tap density of 2.39 g cm^{-3} . Yang *et al.* [88] firstly precipitated 1D microrod $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ using cobalt acetate as starting material, oxalic acid as precipitant. A second precipitation step was proceeded by adding mixed nickel, cobalt and manganese acetate solutions to form $\text{MC}_2\text{O}_4 \cdot x\text{H}_2\text{O}$, which was later mixed with lithium oxalic and underwent an ensuing solid-state calcination step to form final 1D hierarchical microrods. Chen *et al.* [90] synthesized 1D bar-like NCM₄₂₄ by simplifying the synthesis to one step precipitation via preparing $\text{MC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (M = Li, Ni, Co, Mn), followed by a direct calcination step.

(d) hydrothermal [76, 92-97]

Hydrothermal method could prepare products with high homogeneity, diverse morphology, controllable particle size, and high purity [98]. Through careful control of synthesis conditions (*i.e.*, type of solvent, solution concentration, PH value, reaction temperature, reaction time, reaction pressure etc.), NCM could be prepared with various morphologies, such as 3D dumbbell-like NCM₃₃₃ [94], self-assembled NCM₃₃₃ nanosheets [96], single crystal NCM₆₂₂ nanoparticles [99], NCM₃₃₃ hollow microspheres [100], porous hierarchical NCM₃₃₃ nano-/micro spheres [101] etc. However, the hydrothermal usually involves with high pressure, which may raise some safety concerns and is not suitable for industry production.

(e) Spray drying [102-108]

The spray drying method generally requires a relatively short time at relatively lower temperature, but the design of the equipment, processing and the control are considerably difficult. Yue *et al.* [107] reported spray-drying synthesized NCM₆₂₂. Specifically, all the starting materials solutions were firstly fed into a spray-drying equipment to get homogeneously dried precursor, which was then preheated (400 $^{\circ}\text{C}$, air, 5 h), ground in an agate mortar, and calcinated (700-900 $^{\circ}\text{C}$ for 15 h). Similar procedures were also employed to

synthesize $\text{Li}_{1+x}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_{2+\delta}$ by Kim *et al.* [104]. Lin *et al.* [105] used ball milling to get a slurry of Li_2CO_3 , NiO , Co_3O_4 , MnCO_3 and polyvinylbutyral (PVB) in ethanol. The slurry was then spray-dried by a spray-drier, before being calcinated at 900-1000 °C for 10 h.

(f) *Microwave-hydrothermal* [109-113]

Although hydrothermal synthesis can prepare materials with controllable structures, sizes, and morphologies, nevertheless, long reaction time is generally needed in the traditional hydrothermal synthesis route [114]. Microwave has strong penetration ability to be rapidly absorbed by reactant, obtaining sufficiently high temperature needed in a few minutes. Thus, dramatically reduced reaction time spanning from days and hours to minutes and even seconds can be achieved [115]. However, microwave synthesis has difficulty to generate the controllable morphologies and phases. Therefore, the coupled microwave-hydrothermal method, which possesses advantages of both hydrothermal and microwave, allows dramatically reduced reaction time along with controllable morphology, particle size distribution and high purity [110, 116]. For instance, Shen *et al.* [111] prepared submicron sized (0.2-0.3 μm) particles, which are much smaller than those prepared by conventional coprecipitation method (1-3 μm). More importantly, the precursor of $(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})(\text{OH})_2$ was synthesized within greatly reduced reaction time, *ca.*, 20 min (*vs.* 24 h for coprecipitation method).

2.5 Surface Coating

2.5.1 Motivation

To date, NCM cells have become a global mainstream battery technology due to its compromise between high current rate and high capacity. For instance, Tesla roadsters are equipped with $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ as the cathode electrode material and Boeing Corporation uses the NCM_{333} as cathode material for LIBs [117, 118]. Nevertheless, NCM series still suffer from strong capacity fading at higher current densities and/or with pronged cycles [88, 89]. A current trend

with the NCM series is to increase nickel content to achieve higher capacities. However, as discussed in previous section, the onset temperature of oxygen release peaks decreased with increasing nickel content [39]. The release of oxygen can burn the flammable electrolyte, resulting in electrolyte venting, smoke, fire, or explosion and becoming a security hazard. Therefore, the thermal stability of NCM remains as a safety issue [119]. The detrimental electrochemical performance is mainly affected by the surface chemistry and unwanted side reactions at interface of electrode/electrolyte. Therefore, a systematic understanding of surface chemistry and possible side reactions is highly desirable for electrochemical performance improvement.

Figure 2.7 Illustration of surface reactions of nickel rich NCM in (a) exposure to air, and (b) at the interface of electrolyte and electrode [120].

Typically, during the synthesis of NCM cathode materials (especially for Ni-rich series), introducing excess of lithium is quite necessary to: 1) compensate the lithium source loss during calcination step at high temperature; 2) minimize cation mixing (mainly about Ni²⁺/Li⁺ disorder) to form well-

defined layered structure. However, these lithium residues can easily uptake the oxygen, carbon dioxide, and moisture in an ambient environment, forming surface contaminates, *i.e.*, Li_2CO_3 and LiOH (Figure 2.7a) [120, 121]. During the electrode preparation period, after being dissolved into NMP solvent, these surface residual impurities will rapidly form composite gel with high viscosity. Consequently, nonuniform slurry coating with insufficient adhesion between active material and current collector occurs [30]. Owing to the insulating property, these electrochemically inactive surface residues can severely deteriorate the electrochemical performance by behaving like ion/electron blocker. When using standard electrolyte (1M LiPF_6 dissolved in EC and DMC with 1:1 volume ratio, Figure 2.7b), some detrimental side reactions happen spontaneously at the interface between electrode and electrolyte, forming P/O/F containing compounds [117]. LiPF_6 , as a commonly used lithium salt for electrolyte, is very sensitive to water. Even a tiny amount of moisture inside the electrolyte can cause the formation of HF, which is generally responsible for the dissolution of transition metals, surface structure corrosion and phase transformation. All these problems will strongly deteriorate the battery performance. Additionally, at higher operating voltage (~ 4.6 V), the highly reactive Ni^{4+} , Co^{4+} can induce the electrolyte decomposition along with the loss of oxygen, accompanied by structural transition from layered to spinel structure, and to rock-salt structure. Even worse, the released oxygen may trigger some severe safety issues, such as thermal runaway, exhibiting sparks, fires and even explosion [29, 30, 122]. This safety threaten is more severe at higher temperature (> 55 °C) due to accelerated structural instability.

To address these above-mentioned problems, a prominent progress in improving the electrochemical performance has been achieved, a result attributed to the tremendous efforts devoted for surface coating. Ideally, the surface coating layer is capable of prohibiting the direct physical contact of electrode with electrolyte and thus greatly alleviating the undesirable side reactions, such as the dissolution of transition metals, oxygen loss, and phase

transformation [123-125]. As a result of stabilized surface, the structural integrity can be well maintained and meanwhile safety issues can be alleviated. Through a careful selection of coating materials and preparation methods, the electrochemically inactive surface residues of NCM could be reacted into lithium-conductive species. In addition, some coating layers are able to enhance the electronic/ionic conductivity and even the thermal properties.

2.5.2 Summarization of Synthesis Routes

In this section, three types of mostly common used coating synthesis routes, including core-shell structure coating, ultrathin film coating and rough coating, are summarized in Table 2.1 together with their general preparation methods, advantages and disadvantages.

(a) Core-shell structure coating

The core-shell compounds were firstly reported by Amine and Sun *et al.* [32, 126, 127]. The key point here is to use the nickel-rich $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$ as the core and manganese-rich $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ as the shell via two-step coprecipitation and a following calcination step, as illustrated in Figure 2.8. Taking advantages of high capacity from core part and stable structural as well as thermal properties from shell part, the overall compounds showed a remarkable breakthrough in terms of high-energy density, superior cyclability and thermal stability. However, this kind of coating method normally requires more complicated, time-consuming and cost-consuming processing procedures. Besides, the ratio of core to shell needs to be carefully controlled to ensure high performance. The thickness of coating layer is barely maintained at nanoscale, which will retard the mobility of electrons and ions. Additionally, after prolonged cycling (especially at high C rates), the structural mismatch can increase mechanical stress, form cracks and even cause total separation of core from shell, posing a foreseeable threaten of electrochemical performance.

Figure 2.8 Schematic illustration of step-by-step formation process of $\text{Li}[(\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})_{1-x}(\text{Ni}_{0.5}\text{Mn}_{0.5})_x]\text{O}_2$ [126].

(b) Ultrathin film coating

Atomic layer deposition (ALD) is a commonly used technique for ultrathin film coating [128]. In a typical ALD process, the chemical source vapors are brought into the reaction chamber alternately, one at a time, separated by complete purging with an inert gas. Each precursor exposure step saturates the surface, leading to self-limiting film growth [129, 130]. Such a unique reaction mechanism allows the formation of extremely uniform and conformal deposition of thin films. Generally, through controlling the deposition cycles, the film thickness could be precisely controlled at the nanoscale level. Nowadays, researchers have successfully employed ALD technique for various coating materials, such as Al_2O_3 [131, 132], $\text{Al}_2\text{O}_3\text{-Ga}_2\text{O}_3$ [133], ZrO_2 [134, 135], ZnO [136], TiO_2 [137, 138], MgO [139], as protective layers for NCM with marked enhancement in electrochemical performance. However, disadvantageously, the choice of coating materials is quite restricted due to limited deposition sources. The most commonly seen ALD coating materials are metal oxides, which generally show very low electronic conductivity.

Besides, the coating layers prepared by ALD technique are normally dense and continuous. Therefore, to a certain extent, the diffusion ability of Li^+ will be impeded.

(c) *Rough surface coating*

Rough surface coating, which generally includes wet-process coating and dry-process coating, is another commonly employed surface coating strategy. A typical dry-process coating generally involves with mechanical mixing and sequential heating treatment. For instance, Hu *et al.* reported $\text{Co}_3(\text{PO}_4)_2$ and AlPO_4 coated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ by simply mixing $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ with $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) under grinding. Stoichiometric $\text{Na}_3(\text{PO}_4) \cdot 12\text{H}_2\text{O}$ was added under grinding for another 40 min, followed by a heating step (700 °C for 4 h, in air) [140]. Similar synthesis procedures have been used to prepare graphene coated NCM_{333} [141], Li_2MoO_4 -inlaid NCM_{523} [142], MOF-derived alumina coated NCM_{622} [37] etc. The coating layer of dry-process coated samples is normally quite rough and discrete, with some regions heavily coated while other regions barely coated. The wet-process coating generally includes co-precipitation [124], sol-gel [143], hydrothermal [144], solvothermal [145], spray drying [146] methods. Among them, co-precipitation appeals for its advantages, such as low cost, simple procedure and ease for scale-up. Typically, the starting material of coating layer is mixed with NCM in solution under stirring, followed by the adding of precipitants to form suspensions of the coating material. Afterwards, the dried mixture is treated by a heating process to form the final product. The wet-process coating procedure is more complicated than that of dry-process coating, however, yield with more uniform coating layer. Overall, both methods are for ease of operation with low cost, and are feasible for large-scale industrialization.

Table 2.1 Summarization of three common coating strategies, including core-shell coating, ultrathin film coating and rough coating.

Type	Method	Advantages	Disadvantages
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Core-shell	Two-step co-precipitation	Core: high capacity Shell: high stability	Thickness too high; Complex preparation; Structural mismatch; Increased mechanical stress; Formation of cracks;
Ultrathin film	ALD; CVD;	Uniform; Continuous; Nanoscale; Tunable thickness; Precise control;	Limited sources; Impeded conductivity;
Rough	Co-precipitation; Hydrothermal; Solvothermal; Spray drying; Sol-gel; Ball milling;	Simple preparation; Ease for scale up;	Not continuous; Not uniform;

2.5.3 Surface Coating to Improve Electronic Conductivity

Surface coating motivation

Despite of the existing challenges, improving ionic/electronic conductivity is a feasible way to augment capacity, energy/power densities [147]. Most of the currently used cathode materials are transition metal oxides with low electronic and ionic conductivity [147]. For NCM, poor rate performance and inferior cycling stability are the most severe problems that limit its applications. The main purpose of surface modification is to act like a physical protection barrier to prohibit the NCM surface from unwanted side reactions. Consequently, transition metal dissolutions, structure damage and phase

transitions can be suppressed. In some cases, certain surface coating layers are capable of acting as HF scavenger by reacting with the surface moistures. Moreover, an ideal coating layer can not only possess the above-mentioned features but also behave as electron- or/and ion-conductive media to improve reversible capacity upon cycling and enhance rate capability. Herein, different coating strategies have been overviewed in the following sections from the aims of improving electronic or/and ionic conductivity.

Role as electron-conductive media

Electronic conductivity plays a significant role in electrode materials. Surface coating with highly electron-conductive materials is a necessary and efficient strategy for NCM due to the following reasons. 1) The highly electron-conductive coating layer can improve the electron transfer through the interface of NCM particles, accelerating the heterogeneous charge transfer process on the NCM surface [148]. 2) The intimate connection with NCM particles can provide extra electron-conducting pathways among and between the NCM particles and current collectors. According to different types of coating materials, the following discussions are classified into carbonaceous materials and polymers.

(a) Carbonaceous materials

Carbon coating is effective for olivine-type (LiFePO_4) and spinel-type (LiMn_2O_4) cathode materials. Taking LiFePO_4 for example, the electrical conductivity of bare LiFePO_4 is $\sim 10^{-9} \text{ S cm}^{-1}$, much lower than that of LiCoO_2 ($\sim 10^{-4} \text{ S cm}^{-1}$). However, by adjusting the carbon coating amounts, the electrical conductivity can be tuned up to $\sim 10^{-4} \text{ S cm}^{-1}$ (7wt% carbon), $\sim 10^{-3} \text{ S cm}^{-1}$ (17wt% carbon) and $\sim 10^{-1} \text{ S cm}^{-1}$ (30wt% carbon) [147]. Besides, the carbon coating can also reduce primary particle size by suppressing the particle growth, and prohibiting the oxidation of Fe^{2+} to Fe^{3+} during calcination step [118]. However, in the case of NCM, the traditional and widely employed carbon coating is quite a limited choice due to its requirement of air or oxygen atmosphere during the calcination step [149]. At high temperature, the oxygen-contained atmosphere

will decompose the carbon source to form highly reductive byproducts, such as CO or H₂ gases [150]. As a result, the transition metal oxides will be reduced, leading to changes in valence states and even changes in crystal structure. At inert gas atmosphere, carbon material can be protected, however, at the cost of producing oxygen-deficient transition metal oxides.

Realizing the difficulty of conventional methods, researchers tend to find other alternative synthesis routes for carbon coating. Marcinek *et al.* prepared thin layer graphitic carbon coated NCM₃₃₃ via high power microwave plasma chemical vapor deposition (MPCVD). The organic anthracene was put at one side of glass slide as the precursor. Powder NCM₃₃₃ was placed ~5 mm away from anthracene at the other side (Figure 2.9a). Under the argon plasma discharge, the anthracene precursor was rapidly evaporated, pyrolyzed and precipitated on the surface of NCM₃₃₃ powder, forming carbon coated NCM₃₃₃ (Figure 2.9b). A carbon layer (~ 10 nm) was clearly observed from TEM image as shown in Figure 2.9c. The enhanced electrochemical performance of carbon coated NCM₃₃₃ (Figures 2.9d and e) revealed that thin graphite layer assured good electronic contact between cathode particles without hindering Li⁺ transport across the interface. This route involved no thermal decomposition or transformation of NCM₃₃₃ [150]. Recently, Shi *et al.* have synthesized carbon coated Li_{1.048}Mn_{0.381}Ni_{0.286}Co_{0.286}O₂ via a novel magnetron sputtering technique with graphite target as carbon source. At 0.1 C, the carbon coated sample delivered 203.4 mAh g⁻¹ capacity, which is nearly 10 mAh g⁻¹ higher than that of pristine sample. Almost no capacity decay was observed after 50 cycles at 0.1 C, retaining a capacity retention ratio as high as 99.3%. In contrast, only 78% of initial capacity was retained for pristine counterpart. Significant capacity improvement was also achieved at higher current densities (5 C), *i.e.* 145.3 mAh g⁻¹ for coated sample and 103.4 mAh g⁻¹ for non-coated sample.

Figure 2.9 (a) Illustration of MPCVD system; (b) schematic preparation, (c) TEM image of carbon coated NCM₃₃₃; Comparative of electrochemical performance before and after coating carbon: (d) rate and (e) cycling performance [150].

In the past decade, graphene has emerged as a promising conductive medium due to its highly appealing properties, such as the extraordinary electronic conductivity, large surface area and strong mechanical properties [151, 152]. Graphene coating has been widely applied in various fields including but not limited to supercapacitors [153, 154], lithium-ion batteries [141, 155], lithium-sulfur batteries [156, 157] etc. Wu *et al.* reviewed various graphene based metal oxides composites [158, 159]. Raccichini *et al.* gave an overview about roles of graphene played in electrochemical energy storage with six models as shown in Figure 2.10 [160]. The advantages of introducing graphene into NCM are the attractive electronic conductivity as well as the superior thermal stability which can dissipate heat generated from high current loads and/or abuse circumstances [161]. Rao *et al.* have reported NCM₃₃₃-graphene composites through an inversed microemulsion method followed by ball milling process in ethanol [141]. Ascribed to the increased grain connectivity and electronic conductivity, the composites showed the highest

discharge capacity with improved rate capability and cycling performance. Jiang *et al.* have synthesized reduced graphene oxide wrapped NCM₃₃₃ by firstly dispersing rGO in N-methyl-pyrrolidinone (NMP) solution to obtain homogeneous rGO/NMP suspension. The electrode was prepared by mixing the suspension with NCM₃₃₃, carbon black (CB) and poly(vinyl difluoride) (PVdF) [162]. On account of the 3D conducting networks, the graphene coated NCM₃₃₃ demonstrated significantly enhanced rate performance, *e.g.* 110 mAh g⁻¹ (6 C) and 55 mAh g⁻¹ (20 C) was delivered, respectively. On the contrary, no capacity was delivered without graphene coating. Owing to the addition of 3D conductive rGO, both electrochemical impedance spectroscopy (EIS) and potentiostatic intermittent titration (PITT) measurements confirmed that the rate performance was improved by the enhanced electrical conductivity, particularly for the two-phase region. Similar synthesis of graphene-containing NCM₆₆₁₇₁₇ has also been report by Shojan *et al.* [163]. Free-standing Li₂MnO₃•LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ on 3D graphene has been successfully synthesized by Xin *et al.* via *tert*-butanol-assisted freeze-drying process [164]. Advantageously, this novel method avoided transition metal dissolution which is an inevitable problem in water-based method. The 3D porous conductive framework facilitated electronic/ionic conductivities, which undoubtedly improved electrochemical performance. Moreover, the binder-free and current collector-free electrode design can greatly reduce the cost.

Figure 2.10 Schematic graphene based composites models: (a) encapsulated model; (b) mixed model; (c) wrapped model; (d) anchored model; (e) sandwich-

like model; and (f) layered model. Blue: metal oxides particles, Gray: graphene sheets [160].

(b) Electron-conductive polymer materials

Recently, electronic conductive polymers, such as polypyrrole (PPy), poly(3,4-ethylenedioxy-thiophene) (PEDOT), polyamide (PI), poly(ethylene glycol) (PEG) and so on, have been proven to be effective as conducting backbones for electrode materials. For instance, Xiong *et al.* synthesized PPy-coated NCM₈₁₁ by chemical polymerization with Fe³⁺ tosylate as oxidant agent [165]. After coating, a dramatic improvement in electrochemical performance was evidenced even at high temperature (2.8-4.3 V at 60 °C) or high voltage (2.8-4.5 V at 25 °C). With 1.59 wt% of coating PPy, the initial capacity at 0.1 C showed no decrease. The PPy-coated NCM₈₁₁ displayed considerably higher capacity retained at high current densities (10 C), *ca.*, 132.4 *vs.* 115.2 mAh g⁻¹ for the non-coated NCM. At higher temperature (60 °C), considerable improvement was also achieved after PPy coating with 69.8% capacity retention (*vs.* 45.5% of pristine NCM). The enhanced electrochemical performance is attributed to the coating layer of PPy which can mitigate side reactions and facilitate the electron transportation through behaving like an electron conductive protection skin at nanoscale. Due to the excellent electronic conducting property, PEDOT has attracted enormous attention recently as a coating material. Liu *et al.* proposed a facile way by simply mixing NCM₃₃₃ with PEDOT solution, grinding and drying, followed by low temperature heating [166]. Evidenced by the galvanostatic intermittent titration (GITT) and cyclic voltammetry (CV) results, the highly conductive coating layer suppressed cell polarization, and promoted mass transfer at interface between electrode and electrolyte. Although exothermic peak only showed a slight shift from 283.1 °C to 284.6 °C after coating, the heat generated during differential scanning calorimetry (DSC) measurement dropped dramatically (from 129.0 J g⁻¹ to 69.3 J g⁻¹). Consequently, the PEDOT-coated NCM₃₃₃ demonstrated enhanced rate performance and thermal stability.

2.5.4 Surface Coating to Improve Ionic Conductivity

Role as ion-conductive media

Compared with electronic conductivity, ionic conductivity of layered NCM is more sluggish. The most straightforward way to enhance ion diffusivity is to shorten diffusion pathways by reducing particle size to nanoscale. However, nano-sized cathode particles generally show a high reactivity and thus consume more lithium sources in order to form stable cathode electrolyte interface (CEI) layer, resulting in less reversible discharge capacity with lower Coulombic efficiency. Besides, the CEI layer can act as a diffusion barrier to impede Li^+ diffusion, leading to increased polarization and thus poor rate performance. An ionic-conducting coating layer would facilitate ion transfer between electrode and electrolyte by lowering the ion transfer energy barrier. The following section analyzed two efficient ways to improve ionic conductivity through coating Li^+ conductive materials and amorphous materials.

(a) Lithium ion conductive materials

Although noticeable achievements have been fulfilled in surface coating, so far, most of the coating materials are insulators for Li^+ conduction, such as MgO [167], Al_2O_3 [168], Sb_2O_3 [169], Nb_2O_5 [29], ZnO [136], Y_2O_3 [170], Cr_2O_3 [171], AlF_3 [172], MgF_2 [173] etc., which will negatively affect the practical rate performance and cycling stability. Recently, Li-ion conductors including Li_2ZrO_3 [174-178], LiNbO_3 [179], $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [180], Li_2TiO_3 [176, 177, 181, 182], Li_3VO_4 [183-185], LiSnO_3 [181], Li_2SiO_3 [145, 186] and LiAlO_2 [144] etc., have been chosen as surface coating materials for NCM to improve the electrochemical performance (as summarized in Table 2.2). Hu *et al.* reported Li_2SnO_3 coated NCM_{523} with enhanced cycling stability and rate capability [181]. Based on the EIS results, higher Li^+ diffusivity and lower charge transfer impedance were achieved after coating, ensuring improved electrochemical performance. Li_3VO_4 , whose ionic conductivity has been

reported to be $\sim 10^{-4} \text{ S m}^{-1}$, is a good choice of Li^+ conductor. According to Wang's work, Li_3VO_4 -coated NCM_{333} delivered stable cycling performance and significantly improved rate capability (3.0-4.6 V) [183]. Through a novel synchronous lithiation route with LiOH (Figure 2.11a), Zhang *et al.* prepared Li_2ZrO_3 -coated NCM_{333} [174]. TEM images (Figures 2.11b and c) clearly evidenced the successful coating with Li_2ZrO_3 . For the high C-rate performance (Figure 2.11d), the coated sample delivered 106 mAh g^{-1} capacity at 10 C, substantially higher than that of bare material (46 mAh g^{-1}). Figures 2.11e-g showed significantly enhanced cycling stability at a wide operation temperature range, *ca.*, -20 -55°C . The considerable improvement was attributed to the improved velocity of Li^+ migration, reduced charge transfer resistance, reduced cation mixing as well as the doping effect of Zr^{4+} .

Figure 2.11 (a) Schematic illustration of the fabrication of Li_2ZrO_3 -coated NCM_{333} ; (b-c) HRTEM image of Li_2ZrO_3 -coated NCM_{333} ; (d-g) comparative rate and cycling performance of pristine NCM and Li_2ZrO_3 -coated NCM_{333} [174].

Table 2.2 Recent achievements of various lithium conductive coatings for NCM.

Composites	Voltage / V	Rate performance improvement / mAh g^{-1}	Cycling performance improvement / mAh g^{-1}	Interpretation	Ref.
Li_2TiO_3 coated	3.0-4.3	811: 118 (vs. 95) at 10 C; 622: 112 (vs. 70) at 10 C;	811: 90.7% (vs. 82.2%) for 100 cycles at 2 C	Increased ionic conductivity by Ni^{2+} and	[176]

NCM ₈₁₁ , NCM ₆₂₂ , NCM ₄₃₃		433: 88 (vs. 70) at 10 C;	622: 87.2% (vs. 78.0%) for 100 cycles at 2 C 433: 87.7 (vs. 65.0%) for 100 cycles at 2 C	Co ³⁺ doped Li ₂ TiO ₃ ; Suppressed side reactions by Li ₂ TiO ₃ coating layer; 3D Li ⁺ migration path provided by nanobelt Li ₂ TiO ₃ coating layer;	
Li ₂ TiO ₃ coated NCM ₃₃₃	3.0-4.3 3.0-4.6	92.3 (vs. 53.6) at 10 C	90.3% capacity retention after 500 cycles at 20 C (3.0-4.3V); 82.4% (vs. 52.6%) capacity retention after 200 cycles at 1 C (3.0- 4.6V);	Improved Li ⁺ diffusion coefficient after coating (from GITT result); Complete and stable coating shell hindered reduce side effects of Ni ⁴⁺ and Co ⁴⁺ with electrolyte; Ti ⁴⁺ doping enabled enhanced structural stability due to stronger Ti-O bonding;	[177]
Li ₂ TiO ₃ coated NCM ₅₂₃	3.0-4.6	3% LTO@NCM: 136.5 (vs. 99.2) at 5 C; 108.2 (vs. 43.8) at 10 C;	3% LTO@NCM: 92.4% (vs. 74.3%) capacity retention after 100 cycles at 1 C; 83.7% (vs. 63.9%) capacity retention after 100 cycles at 1 C (55°C);	Improved Li ⁺ diffusion coefficient after coating (from CV result); Alleviated metal ions dissolution, phase transformation and improved structural stability due to Li ₂ TiO ₃ coating;	[182]
Li ₂ SiO ₃ coated Li _{1.13} Ni _{0.30} Mn _{0.57} O ₂	2.0-4.8	123 (vs. 59) at a current density of 400 mA g ⁻¹ ;	90% (vs. 73%) capacity retention after 100 cycles at a current density of 100 mA g ⁻¹ ;	Improved velocity of Li ⁺ migration on the surface of electrode after coating (from EIS result); Reduced polarization and retarded voltage decay due to Li ₂ SiO ₃ coating;	[145]
Li ₂ SiO ₃ coated NCM ₅₂₃	2.5-4.5	154.4 (vs. 141.8) at 2 C; 104.4 (vs. 89.8) at 10 C;	80.0% (vs. 62.1%) capacity retention after 200 cycles at 1 C; 87.6% (vs. 81.4%) capacity retention after 100 cycles at 1 C (45 °C);	Improved Li ⁺ diffusion paths and reduced charge transfer resistance; Improved structural stability;	[186]
Li ₂ SnO ₃ coated NCM ₅₂₃	3.0-4.4 3.0-4.5	152 (vs. 135) at 5 C; 134 (vs. 120) at 10 C;	89.2% (vs. 80.0%) capacity retention after 100 cycles at 0.5 C (3.0- 4.4V); 88.7% (vs. 76.8%) capacity retention after 100 cycles at 0.2 C (3.0- 4.5V); 94.9% (vs. 68.3%) capacity retention after 100 cycles at 10 C (3.0- 4.5V);	Improved Li ⁺ diffusion paths and reduced charge transfer resistance (from EIS result); Rendered less reactive toward electrolyte;	[181]
Li ₂ ZrO ₃ coated NCM ₃₃₃	3.0-4.5	106 (vs. 46) at 10 C;	93.8% (vs. 77.6%) capacity retention after 400 cycles at 5 C (25 °C); 85.1% (vs. 37.4%) capacity retention after 400 cycles at 5 C (55 °C);	Improved velocity of Li ⁺ migration and reduced charge transfer resistance (from EIS result); Reduced cation mixing; Doping effect of Zr ⁴⁺ ;	[174]
Li ₂ ZrO ₃ coated NCM ₅₂₃	2.8-4.5	156 at 300 mA g ⁻¹ ;	96.6% (vs. 78.9%) capacity retention after 50 cycles at 60 mA g ⁻¹ (55 °C);	Decreased the mixture of Ni ²⁺ and Li ⁺ and amended the ion transportation; Stable electrode/electrolyte interface and reduced electro- chemical impedance;	[107]
LiAlO ₂ coated NCM ₅₂₃	2.7-4.4 2.4-4.6	158 (vs. 76) at 5 C (2.7- 4.6V);	88.1% (vs. 86.0%) capacity retention after 100 cycles at 1 C (2.7- 4.4V);	Alleviated damage from HF; Retarded oxygen release; Removed surface lithium	[144]

			91.0% (vs. 73.8%) capacity retention after 100 cycles at 1 C (2.7- 4.6V);	residues; Fastened Li ⁺ conductivity; Al ³⁺ ion doping effect;	
Li ₃ VO ₄ coated NCM ₅₂₃	2.8-4.6 2.8-4.8	3wt% Li ₃ VO ₄ coated NCM: 118.0 (vs. 109.1) at 20 C;	3wt% Li ₃ VO ₄ NCM: 63.5% (vs. 51.2%) capacity retention after 100 cycles at 1 C (2.8- 4.6V); 63.0% (vs. 41.5%) capacity retention after 100 cycles at 1 C (2.8- 4.8V); 41.3% (vs. 1.4%) capacity retention after 100 cycles at 10 C (2.8-4.6V);	Improved Li ⁺ conductivity, reduced polarization; Restrained side reactions by Li ₃ VO ₄ layer at high voltages;	[184]
Li ₃ VO ₄ coated NCM ₃₃₃	3.0-4.6	LVO-700 coated NCM: 144.2 (vs. 130) at 5 C; 137.5 (vs.80) at 10 C;	87.5% (vs. 80.3%) capacity retention after 100 cycles at 1 C;	Diminished charge transfer impedance; Suppressed side reactions; Well-crystallized and homogenous coating layer;	[185]
Li ₃ VO ₄ coated NCM ₃₃₃	3.0-4.6	168.7 (vs. 138.6) at 5 C; 159.9 (vs. 92.5) at 10 C;	90.8% (vs. 79.4%) capacity retention after 100 cycles at 1 C	Amended charge transfer impedance; Suppressed side reactions;	[183]

(b) Ion-conductive polymer materials

Apart from lithium conductive metal oxides, some ionic conductive polymers are also attractive as surface coating materials. Owing to the outstanding mechanical, thermal, and chemical stability as well as exceptional film forming ability, polyimide (PI) has been widely used in transistor applications, liquid crystal displays, and membranes [187]. Recently, PI has received intensive attentions in battery applications. For instance, polyimide gel polymer electrolyte nano-encapsulated LiCoO₂ was successfully prepared by Park *et al.* [188]. The ionic conductivity was estimated to be of 0.15 mS cm⁻¹ by swelling PI film with liquid electrolyte. The unique features of PI coating layer, such as facile ion transport, highly conformal surface coverage and nano-sized thickness (~ 10 nm), ensure satisfactory capacities (3.0-4.4 V). By reducing the coating thickness to ~5 nm, the PI coated LiCoO₂ achieved significant improvement in terms of high voltage performance (up to 4.4, 4.5, 4.6 V) and thermal stability [189]. Encouraged by the successful application of PI coated LiCoO₂ materials, Park *et al.* applied similar coating strategy for NCM₃₃₃ via thermal imidization of polyamic acid [190]. Raising the upper cut-off voltage (particularly above 4.6 V) generally entails deterioration of cell performance. The cyclability and safety problems are vitally salient due to undesired

interfacial reactions between the highly delithiated NCM₃₃₃ and reactive electrolytes at high voltage conditions. As expected, with the PI coating layer, the capacity retention ratios at higher cut-off voltages increased from 58% to 71% (2.8-4.6 V) and 52% to 66% (2.8-4.8 V) after 50 cycles at 1 C, respectively. Supported by EIS and CV results, the enhanced electrochemical performance was attributed to the presence of PI layer which can effectively prevent the formation of undesired resistive layer from accelerating the resistance growth. Particularly, due to the stable thermal and chemical properties, the thermal stability of PI coated NCM₃₃₃ was significantly enhanced, evidenced by DSC measurements. In detail, the exothermic heat generated decreased from 525 J g⁻¹ to 338 J g⁻¹, meanwhile, the exothermic peak shifted from 278 °C to 298 °C in the voltage range of 2.8-4.6 V. When charged to 4.8 V, although a decline in thermal stability was observed, the PI coated samples still showed superior thermal tolerance compared to pristine sample with 307 J g⁻¹ less heat generated and 5 °C higher exothermic peak shifting.

As aforementioned that the nickel-rich NCM is very sensitive to moisture [165]. The presence of HF in the electrolyte can severely dissolve transition metals. Wang *et al.* firstly reported ethoxy-functional polysiloxane (EPS) coated NCM₆₂₂ [40] via the *in situ* hydrolysis-condensation polymerization of tetraethyl orthosilicate (TEOS) (Figure 2.12a). Due to the property of high sensitivity to acid, alkali and H₂O, TEOS can easily react with surface moisture and scavenge HF in the liquid electrolyte to form organic polysiloxane. The electrochemical performance results (Figures 2.12b-d) revealed that the cycling stability was enhanced with increased coating amount, however, at the sacrifice of capacity loss. If the coating thickness is too high, instead, the hindered lithium ion mobility can lead to inferior rate capability. When increasing the temperature from 25 °C to 55 °C, 2mol% EPS coated NCM₆₂₂ composites delivered 175 mAh g⁻¹ capacity with 84.9% retained capacity after 100 cycles at 1 C. The improved thermal stability was validated by DSC measurement with 16 °C of exothermic peak shift to higher position. By *ex situ* TEM measurement

(Figures 2.12e-g), a thinner and homogeneously distributed CEI layer was observed for EPS coated NCM₆₂₂ with more uniform and smoother surface, leading to significantly improved cell performance with respect to the pristine counterpart.

Figure 2.12 (a) Schematic illustration of the fabrication of EPS-coated NCM₆₂₂ microsphere; (b-d) comparative rate and cycling performance of pristine NCM and E-NCM; HRTEM image of E-NCM (e) before and (g) after cycling; (f) HRTEM image of pristine NCM after cycling [40].

(c) Amorphous materials

Amorphous phases, like grain boundaries, are known to have larger diffusivity than crystalline phases. Thus, diffusivity can be tailored by

controlling the ratio between crystalline and amorphous phases [147]. Recently, MOFs, a class of highly porous materials assembled by the coordination of metal ions and organic ligands, have attracted great attention in electrochemical applications. Amorphous MOF derived alumina coating of NCM₆₂₂ was prepared using NH₂-MIL-53 as precursor by Li *et al.* [37]. The thickness of this amorphous coating layer was estimated to be ~5-7 nm based on TEM images. By adjusting the coating amount of MOF derived alumina, the rate performance was significantly enhanced, especially at higher current densities. For example, surface modified NCM₆₂₂ retained 170 mAh g⁻¹ (5 C) and 150 mAh g⁻¹ (10 C), much higher than those of pristine NCM₆₂₂ (143 mAh g⁻¹ at 5 C, 120 mAh g⁻¹ at 10 C), indicating that the amorphous coating layer facilitated the Li⁺ insertion and extraction abilities.

Metal phosphates series, such as AlPO₄ [122, 191-194], Co₃(PO₄)₂ [30, 140], CoPO₄ [195], NiPO₄ [196], LiPO₄ [197], Mn₃(PO₄)₂ [124], CePO₄ [198], and NaTi₂(PO₄)₃ [199] etc., have been frequently used as coating layers for NCM owing to their strong covalent bonding of P=O as well as good chemical resistance facing of acidic electrolyte. Therefore, metal phosphate coating is expected to improve the cycling stability and thermal stability with long cycling lifetime. Herein, some examples using ultrathin amorphous materials not only as Li⁺ conductive coating layer but also as thermal tolerance layer will be discussed. By modulating the PH value of coating solution, the electrochemical performance of Li₃PO₄ coated NCM₄₃₃ was tuned by Song *et al.* [197]. Specifically, the best cycling and rate performance were achieved when decreasing the PH value of coating solution to 2. Lee *et al.* reported Ni₃(PO₄)₂ coated LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ with coating thickness of 10-20 nm via simply ball milling process [196]. At 10 C, the Ni₃(PO₄)₂ coated LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ delivered 22 mAh g⁻¹ higher capacity than that of pristine LiNi_{0.8}Co_{0.15}Al_{0.05}O₂, indicating that the amorphous coating layer functioned as a booster for lithium ion transportation. When tested at 55 °C, 73% of initial capacity was maintained after 100 cycles (0.5 C), much higher than pristine material (53%). Based on the

EIS results, greatly suppressed growth of charge transfer resistance was observed upon cycling after coating. Moreover, through various *ex situ* characterizations including XRD, SEM and TEM, well maintained layered structure with good morphology integrity was obtained due to the prevented surface degradation by surface coating.

Interestingly, metal phosphates coating is also employed to consume surface residual impurities of NCM materials. Unlike normal coating procedure with relatively low heating temperature, this particular coating strategy requires high heating temperature to promote the reaction of metal phosphates with LiOH and Li₂CO₃ to form olivine type lithium conductive metal phosphates [140, 200]. For instance, Kim *et al.* reported Co₃(PO₄)₂ coated LiNi_{0.8}Co_{0.16}Al_{0.04}O₂ via a typical wet-chemical process [30] with improved electrochemical performance. After heating at 700 °C for 5 h, the lithium contained surface residues were consumed, concurrently with the formation of Li_xCoPO₄. After being dissolved in water, the PH value suddenly dropped from 12.5 to 10.5, providing a direct evidence that the alkaline surface residues were reacted during the annealing process. Moreover, being charged to 4.3 V, no phase transition was observed for the Li reactive Co₃(PO₄)₂ coated LiNi_{0.8}Co_{0.16}Al_{0.04}O₂ after 7 days' storage time at 90 °C. In contrast, the bare LiNi_{0.8}Co_{0.16}Al_{0.04}O₂ was transformed into the spinel phase, possibly as a result of the dissolution of Ni⁴⁺ ions into the electrolytes.

2.5.5 Surface Coating to Improve Electronic/Ionic Conductivity

PEDOT is highly conductive for electrons and PEG has excellent ionic conductivity. Therefore, Kim's group combined these two polymers to form dual-conductive polymer (PEDOT-*co*-PEG) coated NCM₆₂₂ [31]. The copolymer coated composites provided higher capacity, more stable cyclability and improved rate capability. Based on this successful trial, Kim's group prepared double layer coated NCM₆₂₂ with Al₂O₃ nanoparticles and PEDOT-*co*-PEG copolymers [36]. By this design, the thermal stability and safety property

were greatly enhanced. Li *et al.* reported a hybrid Li_xAlO_2 and $\text{Li}_x\text{Ti}_2\text{O}_4$ coated NCM_{811} (LTAO) by a hydrolysis assisted coating process [201]. Li_xAlO_2 nanosheets acted as a Li ion conductor while $\text{Li}_x\text{Ti}_2\text{O}_4$ nanoparticles acted as superconductors [202-204]. The homogenous and conformal hybrid coating membrane provided a “highway” for both Li^+ and electrons, thus yielding greatly promoted rate performance. Another advantage of this coating process is that no extra lithium source was added except for the lithium residuals, such as LiOH and Li_2CO_3 on the surface of NCM_{811} .

Chapter 3

Experimental Methodology

This chapter summarizes all the experimental methods in details, including material synthesis, electrode preparation, cell fabrication, and ex situ or in situ sample preparation for analysis. In addition, instruments related to material characterization and electrochemical testing are also listed, together with their working principles.

3.1 Material Synthesis

3.1.1 Synthesis of 1D Bar-like NCM₄₂₄

Figure 3.1 illustrates the synthesis route of 1D bar-like NCM₄₂₄. AcLi (22 mmol), Ni(Ac)₂·4H₂O (8 mmol), Co(Ac)₂·4H₂O (4 mmol) and Mn(Ac)₂·4H₂O (8 mmol) were firstly dissolved in 200 mL of de-ionized water (DIW) and ethanol (DIW: ethanol = 1: 4 v/v) under continuous stirring until a transparent solution (*A*) was obtained. Meanwhile, H₂C₂O₄·2H₂O (31 mmol) were dissolved in 200 mL of DIW and ethanol (DIW: ethanol = 1: 4 v/v) under continuous stirring until the transparent solution (*B*) was obtained. Afterwards, solution *B* was added into solution *A*, under continuous stirring for 6 h (R.T.). The mixture suspension was then dried at 60 °C to form the MC₂O₄·2H₂O precursor having the 1D bar-like morphology. Four batches of precursors were firstly pre-heated at 450 °C for 10 h and then calcined at 750, 800, 850 or 900 °C for 20 h in a muffle furnace (air atmosphere) to obtain the final product, respectively.

Figure 3.1 Schematic illustration of synthesis route of 1D bar-like NCM₄₂₄.

3.1.2 Synthesis of NCM₆₂₂

Figure 3.2 illustrates the synthesis route of NCM₆₂₂, which was quite similar to that of NCM₄₂₄, except for different amounts of starting materials, *ca.*, LiAc (22 mmol), Ni(Ac)₂·4H₂O (12 mmol), Co(Ac)₂·4H₂O (4 mmol), Mn(Ac)₂·4H₂O (4 mmol) and H₂C₂O₄·2H₂O (31 mmol). And the precursor MC₂O₄·2H₂O was firstly pre-heated at 450 °C for 10 h followed by a

calcination step in a muffle furnace at 800 °C for 20 h in air atmosphere.

Figure 3.2 Schematic illustration of synthesis route of NCM₆₂₂.

3.1.3 Synthesis of MnPO₄-coated NCM₄₂₄/ NCM₆₂₂

For the MnPO₄ coating, an appropriate amount of Mn(Ac)₂·4H₂O was dissolved in deionized water (DIW; 10 mL) before adding the as-synthesized NCM (NCM₄₂₄ or NCM₆₂₂, 1 g) under continuous stirring (Suspension *A*). Meanwhile, a stoichiometric amount of NH₄H₂PO₄ was dissolved in DIW (10 mL, Solution *B*). Solution *B* was subsequently added dropwise to Suspension *A* within 3 h of continuous stirring using a syringe. The suspension mixture was dried at 60 °C by a rotary evaporator. The remaining solid powder was transferred to a muffle furnace and subjected to 300 °C for 5 h (in air, 2 °C min⁻¹) to obtain MnPO₄-coated NCM (MP-NCM). To study the effect of the coating thickness, for MP-NCM₄₂₄, three different samples were prepared with varying MP weight ratios, *i.e.*, 1, 2, and 3 wt% - herein referred to as MP-NCM-1wt%, MP-NCM-2wt%, and MP-NCM-3wt%, respectively. For MP-NCM₆₂₂, only 1wt% coated sample was prepared, herein referred to as MP-NCM.

3.2 Electrode Preparation

3.2.1 Conventional Electrode with Organic PVdF-based Binder

All the PVDF-based electrodes were prepared with the same active material/super carbon/binder weight ratio, *i.e.*, 80:15:5. First, the active material and the carbon additive (C-ENERGY Super C65) were grind-mixed manually in an agate mortar. This step was needed to optimize the carbon dispersion around

the active material particles. Poly-vinylidene fluoride (PVDF 6020, Solvay) was dissolved in an appropriate amount of N-methyl-2-pyrrolidone (NMP, Aldrich). The mixture of active material and carbon was added and subjected to stirring for 6 h. The paste was then casted on Al foils by doctor-blade technique, followed by immediate drying at 60 °C in an oven. Afterwards, disc electrodes (12 mm in diameter) were punched and further dried under vacuum at 100 °C for 8 h. These disc electrodes were pressed at 9 tons cm⁻² for 10 s to increase electrode density for cell assembly.

3.2.2 Conventional Electrode with Aqueous CMC-based Binder

The electrodes were prepared with same ratios, *ca.*, 80 wt% of NCM, 15 wt% of Super C45, and 5 wt% of binder. For the preparation of CMC-based NCM₄₂₄ electrodes (CMC/NCM), sodium carboxymethyl cellulose (CMC, Dow Wolff Cellulosics, Walocel CRT 2000 PPA 12) was firstly dissolved into deionized water (DIW) under stirring for 30 min to form a homogeneous solution. Super C45 (IMERIS) was added under vigorous stirring for 2 h. Afterward, the active material was added together with one drop of phosphoric acid (Sigma Aldrich), and mixed for additional 2 h. The obtained slurries were casted on alumina foils by doctor-blade technique. The coated electrodes were dried at 80 °C. Afterwards, disc electrodes (12 mm in diameter) were punched before being vacuum dried at 170 °C for 12 h for use. These disc electrodes were also pressed at 9 tons cm⁻² for 10 s to increase electrode density for cell assembly.

For the full cells, the graphite (SLP30, TIMCAL) anodes were prepared by dissolving CMC in deionized water. After complete solvation, the required amount of Super C45 was added under continuous stirring. A dispersing system (Dispermat VL, VMA GMBH) was used for further stirring (stirring speed: 2000 rpm, 4 h). Subsequently, a required amount of SLP30 was added and the aqueous mixture was kept under stirring for another 3 h. Before coating the slurry on copper foil, a lower stirring speed (200 rpm) was applied under

vacuum for 10-30 min to remove all the bubbles. The subsequent drying was conducted analogously to the cathode preparation. The graphite anodes had an overall electrode composition of 92 wt% SLP30, 4 wt% conductive carbon, and 4 wt% CMC. The average active material mass loading of electrodes is $3.2 \pm 0.2 \text{ mg cm}^{-2}$.

Table 3.1 Summarization of electrode compositions involved in the thesis.

Electrode Composition	Electrode	Solvent	Active Material
	Composition Ratio		Loading / mg cm^{-2}
Conventional electrode	NCM ₄₂₄ /PVdF/Super C65	NMP	~2
	MP-NCM ₄₂₄ /PVdF/Super C65	NMP	~2; ~4; ~6
	MP-NCM ₆₂₂ /PVdF/Super C65	NMP	~2; ~12;
	NCM ₄₂₄ /CMC/Super C45	H ₂ O	~2; ~4;

3.3 Cell Fabrication

3.3.1 Two-electrode Half Coin Cells

CR2032 coin cells (Figure 3.3) were fabricated in an argon-filled glove box ($\text{O}_2 < 0.1 \text{ ppm}$ and $\text{H}_2\text{O} < 0.1 \text{ ppm}$). Lithium metal (battery grade, Rockwood Lithium) was used as anode. The electrolyte (supplied by BASF) is composed of 1M LiPF_6 dissolved in EC–DMC (1:1 v/v), and 1wt% of vinylene carbonate (VC) as additives. A single layer polyethylene membrane (ASAHI KASEI, Hipore SV718) was used as separator.

Figure 3.3 Schematic illustration of a two-electrode CR2032 coin cell.

3.3.2 Three-electrode Swagelok Cells

One major advantage of the three-electrode Swagelok cell (Figure 3.4), which is also called T-cell, compared to a two-electrode pouch cell is the use of the reference electrode. With the reference electrode, in fact, each half-cell potential (*i.e.*, CE *vs.* RE and WE *vs.* RE) can be precisely monitored. Three-electrode Swagelok type cells were also fabricated in an argon-filled dry box ($\text{H}_2\text{O} < 1$ ppm, $\text{O}_2 < 0.1$ ppm). For SLP 30 graphite half cells, metallic lithium (battery grade, Rockwood Lithium, 0.5 mm) was served as both counter and reference electrodes. For MP-NCM half cells, coin 2032 cells were assembled with lithium metal as the counter electrode. The full cells were assembled using SLP 30 graphite as the anode material, MP-NCM as the cathode material, lithium metal as the reference electrode, 1M LiPF_6 dissolved in EC-DMC solvent (1:1 v/v) with 1 wt% of additive of VC as the electrolyte (BASF), and glass fiber (Whatman, GF/D) as separator. The average areal loadings of the MP-NCM electrodes were $6.2 \pm 0.2 \text{ mg cm}^{-2}$, while the mass loadings of SLP 30 graphite were $3.2 \pm 0.2 \text{ mg cm}^{-2}$.

Figure 3.4 Schematic illustration of a three-electrode Swagelok cell.

3.4 *In situ* Sample Preparation for HT-XRD Analysis

In situ, high-temperature XRD (HT-XRD) measurements were conducted using a Bruker D8 Discover instrument (heating rate: $1\text{ }^{\circ}\text{C s}^{-1}$, Cu-K α radiation, $\lambda = 0.15406\text{ nm}$). Prior to the measurements, the charged electrodes (4.3 V) were transferred to the heating stage and then sealed with a graphite dome, which is connected to a mechanical pump to ensure vacuum during the measurement. The first and second diffractograms were performed at $30\text{ }^{\circ}\text{C}$ and $50\text{ }^{\circ}\text{C}$, respectively while the following were recorded at temperature increments of $50\text{ }^{\circ}\text{C}$, *i.e.*, at $50, 100, 150\text{ }^{\circ}\text{C}$, etc.

3.5 *Ex situ* Sample Preparation

For all the *ex situ* analyses related with conventional electrodes, the cells, regardless of coin cells or Swagelok cells, were opened in the glove box, washed three times by dimethyl carbonate (DMC) solution, dried and stored in the glove box for later usage.

3.6 Instruments

3.6.1 Physico-chemical Property Characterization

(a) X-ray Diffraction (XRD)

XRD is a widely used for the determination of structure and composition of the crystalline materials. As illustrated in Figure 3.5a, a typical set-up of X-ray powder diffractometry includes X-ray tube, sample, incident and diffracted beam optics, and X-ray detector. In the X-ray tube, electrons are emitted from the heated cathode filament, and then accelerated by applying high voltage collide with the anode, generating X-rays. The anode is usually made from a high purity metal, *ca.*, Cu or Mo. After being monochromated and collimated, the X-rays would interact with atomic planes of the crystalline sample and then produce destructive or constructive interferences (Figure 3.5b) following the Bragg's law (Eq. 3.1):

$$n\lambda = 2d \cdot \sin\theta \quad \text{Eq. 3.1}$$

Where n is the integer ($n = 1, 2, 3...$), λ is the wavelength of the X-ray radiation, θ is the diffraction angle, and d is the lattice spacing of the crystalline sample. While the sample is scanning at increased diffraction angles, X-ray detector records and processes the intensity of the diffracted X-rays. By putting the information together on various sets of reflecting planes, the crystal structure determinations can be generated.

Figure 3.5 (a) Basic set-up for X-Ray powder diffractometry, (b) scheme of Bragg's law.

(b) *Scanning Electron Microscopy (SEM) & Energy Dispersive X-ray Spectroscopy (EDS)*

SEM is a widely used to characterize morphology and topography of a solid specimen. The electron beam, generating by an electron gun, *i.e.*, tungsten filament, is focused by (magnetic) electron lenses and accelerated towards the sample surface, as illustrated in Figure 3.6a. When the high-energy electron beam scans a defined area of the specimen, its electrons will interact with the sample's surface, inducing a variety of signals that include Auger electrons, secondary electrons, backscattered electrons and characteristic X-rays. The latter three signals are of primary interest. Their generation at the substrate, occurring in the so-called "electron interaction volume", is schematically illustrated in Figure 3.6b. Secondary electrons are electrons which have been ejected from near surface atoms with energy around 50 eV by the incident electron beam (inelastic scattering). Because of the very limited scale in escape depth (a few nanometers), the secondary electrons are most widely used for high-resolution topographical surface images. After the production of secondary electrons, Auger electrons are emitted as a result of sample de-energization. Due to the feature with element-specific energies, Auger electrons are collected to investigate the compositions of samples. Backscattered electrons are generated over a larger "electron interaction volume" and possess a higher intrinsic energy, with respect to secondary electrons. The number of backscattered electrons correlates to the atomic number of the sample's atoms, variations in the resulting images grayscale of the investigated material reveal different phases. The brighter region is generally associated with elements that possess higher atomic numbers. Therefore, the background electrons are beneficial for compositional information in multi-phase samples with different contrast. Characteristic X-rays are emitted from a depth up to a micrometer. The incident beam creates vacancies by ejecting inner shell electrons which are immediately occupied from an outer shell electron by simultaneously emitting energy in form of X-rays, which are detected by an energy-dispersive detector (EDS) and give information about the specimen's chemical nature.

Figure 3.6 (a) Basic set-up of SEM, (b) schematic depiction of “electron interaction volume”.

(c) High Resolution Transmission Electron Microscopy (HR-TEM)

TEM works with the same basic principles as optical microscope, but uses electrons instead of light. The high energy electrons, generated from electron gun (*ca.*, 200 kV accelerating voltage in our case), behave like a wavefront which has a million times shorter wavelength about than that of lightwaves. They pass through a combination of condenser lens and apertures (Figure 3.7). Passing through a thin region of the targeted material, partial of electrons are transmitted while partial of them are diffracted. A complicated system of electromagnetic lenses focalizes the transmitted electrons into an image, a diffraction pattern, or a nano-analytical spectrum, relying on the operation mode. Each mode provides a different insight about the specimen. For example, the imaging mode presents a highly magnified image of sample region. In order to increase the intensity and the contrast of image, an amplitude contrast could be obtained via elimination of diffracted beam. The atomic arrangements could be visually evidenced when operating in the high-resolution imaging mode. The diffraction mode offers precise information of the regional crystal structure. The nanoanalytical modes (X-ray and electron spectrometry) provides information

about the existence of elements within a tiny volume of material.

Figure 3.7 (a) Basic set-up and (b) working principle of HR-TEM.

(d) X-ray Photoelectron Spectroscopy (XPS)

XPS is a widely used electron spectroscopy technique for surface analysis (2-10 nm), which is capable of identifying elemental composition, the nature of chemical bonds, and elemental valence status. As depicted in Figure 3.8a, XPS detects photoelectrons emitted from a specimen's surface upon X-ray irradiation by a monoenergetic X-ray beam (Mg-K α or Al-K α), due to the photoelectric effect. The photoelectric effect relies on the phenomenon that incident photons interact with the sample element's electrons, leading to the emission of characteristic photoelectrons (photo-ejected electrons). Figure 3.8b schematically illustrates the photoemission principle. The XPS analyzer detects the photoelectrons' KEs and subsequently the BEs can be calculated based on the following Eq. 3.2:

$$KE = h\nu - BE - e\phi \quad \text{Eq. 3.2}$$

Where KE is the kinetic energy of photoelectron, $h\nu$ is the energy of the incident X-ray photon, BE is the binding energy of the respective element's core electron and $e\phi$ is the spectrometer's specific work function (represent the

minimum energy required for electron to escape from the device).

Figure 3.8 (a) Basic set-up and (b) photoemission process involved for XPS surface analysis.

(e) *Thermogravimetric Analysis (TGA)*

TGA analysis is commonly used to evaluate the thermal stability of a material or composite. The sample burning is simulated by heating up or cooling down at a specific heating/cooling rate in a predetermined temperature interval using an electrical furnace under controlled dynamic atmosphere (*e.g.*, nitrogen or oxygen). Prior to measurement, the sample is purged by inert gas. The sample weight change, which could be related to sample surface's adsorption/desorption processes, decomposition, pyrolysis, evaporation, sublimation etc., is recorded upon temperature increase by a high-precision balance with a standard empty pan as the reference (Figure 3.9). Thereby information about the material's thermal stability could be obtained by the degradation temperature. For a composite, due to the different thermal stability of each component, the weight composition of the composite can be obtained based on the different weight loss stages.

Figure 3.9 (a) Basic set-up of TGA.

(f) Differential Scanning Calorimetry (DSC)

DSC is commonly used technique for thermal property investigations. Typically, it measures the difference in terms of heat flow between the sample and the reference, the latter is generally an empty Al pan (Figure 3.10a). Because of the testing conditions, *ca.*, constant pressure and constant heat/cooling rate, thus, the heat flow change is equivalent to the enthalpy change. Therefore, such a technique is frequently employed to examine the endothermic and/or exothermic processes, in both qualitative and quantitative ways. Furthermore, it can provide insights about the glass transition (T_g), melting (T_m) and crystallization (T_c) temperature, as depicted in Figure 3.10b.

Figure 3.10 (a) Basic set-up of DSC, (b) schematic DSC curve with various possible phase transitions.

3.6.2 Electrochemical behavior Characterization

(a) Electrochemical Impedance Spectroscopy (EIS)

EIS measurement is generally conducted to study the intrinsic electrochemical behavior of a galvanic cell, allowing the analysis of the processes within electrodes, such as the contributions from kinetics, double layer, diffusion, etc. EIS tests allow the operations in two modes, e.g., potentiostatic and galvanostatic mode [205]. In potentiostatic mode, by applying a small sinusoidal AC voltage within a wide frequency range, the resulting cell current can be recorded. While, in case of the galvanostatic mode, a small sinusoidal AC current is applied, instead of voltage, and then measure the generated battery voltage. Taking the potentiostatic mode for example, in a

typical EIS measurement, a small sinusoidal perturbation (potential, as shown in Eq. 3.3 and Figure 3.11a) is applied to the system.

$$E_t = E_0 \sin(\omega t) \quad \text{Eq. 3.3}$$

where E_t is the potential at time t , E_0 the amplitude of the perturbation signal, ω the radial frequency which can be expressed by Eq. 3.4.

$$\omega = 2\pi f \quad \text{Eq. 3.4}$$

The sinusoidal (pseudo-linear) response (I_t) is derived from the applied signal in phase (ϕ) and amplitude (I_0), as shown in Eq. 3.5 and Figure 3.11b.

$$I_t = I_0 \sin(\omega t + \phi) \quad \text{Eq. 3.5}$$

The impedance is determined by ratio of potential E_t and current response, Following Ohm's Law (Eq. 3.6).

$$Z(\omega) = \frac{E_t}{I_t} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \phi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \phi)} \quad \text{Eq. 3.6}$$

The complex $Z(\omega)$ can also be expressed as Eq. 3.7, composing of a real and an imaginary part:

$$Z(\omega) = Z_0(\cos \phi + j \sin \phi) \quad \text{Eq. 3.7}$$

where j is the imaginary component ($\sqrt{-1}$).

Figure 3.11 (a) sinusoidal potential perturbation, (b) current response.

Prior to the introduction of a EIS spectrum, a brief summary of commonly used electrical circuit elements is presented. The resistor (R), which is

determined solely by the ratio of amplitudes of potential and current (Eq. 3.8), is associated to the real part of the impedance.

$$Z_R = \frac{\phi_0}{I_0} \quad \text{Eq. 3.8}$$

The capacitor (C) and inductor (L) are described by the imaginary part, which can be calculated based on Eq. 3.9 and Eq. 3.10, respectively.

$$Z_C = \frac{\phi_C}{I_C} = \frac{1}{i\omega C} \quad \text{Eq. 3.9}$$

$$Z_L = i\omega L \quad \text{Eq. 3.10}$$

The constant phase element (CPE) can be considered as a more realistic representation of a capacitor, since it takes the double layer's non-ideal behavior into account by two additional parameters n and T

$$Z_{CPE} = \frac{1}{T(i\omega)^n} \quad \text{Eq. 3.11}$$

Where T has the numerical value of the admittance (Z^{-1}) at $\omega = 1 \text{ rad s}^{-1}$, thus eliminating the dependency of the CPE on the frequency. For $n = 0$, the imaginary term in the brackets becomes 1 and the CPE solely has a real contribution, constituting a resistor ($R = Z^{-1}$). In contrast, if $n = 1$, the CPE becomes a pure capacitor, however, reasonable values of n usually range between 0.6 and 1 [206].

A typical Nyquist plot (Figure 3.12) presents the imaginary part ($-Z_{Im}$) vs. real part (Z_{Re}). The Nyquist plot shows four characteristic processes, as revealed by the Segment I-IV (marked as Seg I-V, Figure 3.12). Panel a in Figure 3.12 is the equivalent series resistance (ESR). Seg I as shown in Figure 3.12b shows a nearly straight-line perpendicular to X-axis, which indicates a typical inductive behavior (L). The intersection of real part (Z_{Re}) in the X axis is the internal resistance (R_e), a combination of total resistance from electrolyte, electrodes, separator. Seg II is associated with the solid electrolyte interphase (SEI, denoted as R_{SEI}) formation. Seg III represents the charge transfer (R_{CT}) resistance at the electrodes. The straight line at low frequencies shows an angle of 45° , is the so-called Warburg impedance (W) regarding the diffusion process. Depending on the frequency of the sinusoidal input signal, as broad rule, the impedance

phenomena occurring at a LIB electrode can be divided in three parts: the high frequency region (>100 kHz, related to ionic or electronic conductivity), the mid-frequency region (100 kHz - 1 kHz, related to passivation layer formation and charge transfer resistance), and the low frequency (<1 kHz, related to bulk diffusion).

Figure 3.12 A typical Nyquist plot showing four characteristic processes in LIBs.

(b) Cyclic Voltammetry (CV)

As a potentiodynamic analysis technique, CV mainly provides information in terms of thermodynamics and kinetics reactions within electrodes. However, the application possibilities for CV measurements are not limited to solely electrode materials but can also to other battery components, like separator and electrolyte. However, in this thesis, we only focus on the CV test for electrode (active material) reactions. In a typical CV measurement, a potential (excitation signal) that changes linearly with time by a selected constant scan rate (Figure

3.13a) is applied between the WE and CE. Reaching a certain potential (switching potential), the sweep direction is reversed. This results in a triangular shaped waveform of the excitation signal (Figure 3.13a). Upon scanning, the current flow between the WE and CE is detected. Scanning rates are determined by different systems, types of electrode materials and the study purposes.

Figure 3.13 (a) Potential linear varied as a function of scanning time, (b) a typical CV curve.

Figure 3.13b displays a typical CV curve that illustrates the potential *vs.* the current flow, where the redox dots marked from A to G correspond to the points selected in Figure 3.13a. The electron transfer during a redox reaction is reflected by characteristic peaks in the CV. Herein, the cathodic peaks are corresponding to the reduction reaction, while the anodic peaks represent the oxidation reaction. From the peak shape, position and number, information on the material's crystallinity (sharp *vs.* broad peaks), the reversibility of the redox processes and the number of involved electrons, can be derived. Moreover, due to the time dependence of the excitation signal, electrode kinetics as well as charge carrier diffusion can be determined by varying the scan rate. For instance, a multi-scan rate test is commonly used for the calculation of lithium ion apparent diffusion coefficient, which will be explained in chapter 4 in detail.

Table 3.2 Summarization of detailed information about all the techniques involved in the thesis.

Techniques	Manufacture brand/model	Test information details
XRD	Brucker D8	Cu K α radiation, $\lambda=0.15406$ nm
SEM	ZEISS EVO MA10	/
HR-TEM	JOEL UHR 2010 JOEL 2100F	200 kV
EDS	JOEL 2100F	200 kV
XPS	PHI 5800 Multi- Technique System	Monochromatic Al K α source radiation, 1486.6 eV
TGA	TA Instruments Discovery Model Q2000	/
DSC	TA Instruments Discovery Model Q2000	/
EIS	VMP Biologic-Science Instruments	/
CV	VMP Biologic-Science Instruments	/

Chapter 4

1D Bar-like NCM₄₂₄ as a Stable Cathode Material for Lithium-ion Batteries with Superior Long-term Capacity Retention and High Rate Capability

In this chapter, we present the successful synthesis of 1D bar-like NCM₄₂₄ (N-NCM), preferentially exposing the {010} electrochemical active facets. The material is obtained via a precipitation process followed by a calcination step. Through an optimization of calcination temperature, we obtained the optimal sample (NCM-800), which processes significantly enhanced lithium ion diffusivity, superior C-rate capability, and stable cycling performance. These are attributed to the synthesis design strategy leading to 1D bars with preferentially exposed {010} electrochemical active facets, which provide more open structure for unimpeded Li⁺ migration. In addition, the diffusion pathway of lithium ions is greatly reduced because of the bar shape morphology. What's more, the synthesis method we chose here is very simple, low cost and ease for scaling up, which appeal for the industry production interests.

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4.1 Introduction

Electrochemical energy storage and conversion systems, which can offer solutions towards globally greener and sustainable energy future, play a momentous role in our daily life [207, 208]. Nowadays, lithium ion batteries (LIBs) are considered among the most feasible candidates for energy storage systems of portable electronic devices, electric vehicles (EVs) and hybrid electric vehicles (HEVs) [209, 210]. However, driven by the market demands, next generation LIBs with higher capacity, energy density, and rate capability, longer cycling lifetime and lower cost, are under intense explorations [32]. In this regard, Ni-rich ($\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$, nickel-rich NCM) and lithium- and manganese- rich ($x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$, LMR-NCM) cathode materials are among the most promising competitors owing to their high capacity and specific energy combined with relatively low cost [211, 212]. While LMR-NCM with layered structure can deliver high specific capacity (*ca.*, 250 mAh g^{-1} at C/10 rate), these materials face some intrinsic challenges, such as: 1) unavoidable voltage decay due to the continuous irreversible phase transformation from layered to spinel structure [22-24]; 2) release of oxygen due to the activation of Li_2MnO_3 over 4.5 V during the initial delithiation process, which poses a serious safety issue [25, 213]; and 3) electrolyte decomposition because of the wide working voltage range (2.5-4.8 V). These features give rise to eventual severe capacity degradation, energy density decay and poor rate capability, which are still to be overcome [26]. On the other hand, nickel-rich NCMs have recently attracted enormous attention as they exhibit higher capacity and lower cost as compared to the commercial NCM₃₃₃ due to the increased fraction of the electrochemically active element (Ni). However, the increased nickel content (especially when $1-x-y > 0.5$) has, according to some reports, resulted into more severe capacity deterioration, due to thermal and structural instabilities caused by Ni^{2+} ions migration into Li^+ sites [27] because of their similar radii. NCM₄₂₄, which achieves moderately high specific capacity ($\sim 160 \text{ mAh g}^{-1}$ at C/10 rate within 3.0-4.3 V) with relatively low cation

mixing and quite stable structure [214], seems to present an attractive proposition. Nevertheless, the issues of inferior rate capability and poor long-term cycling stability of NCM₄₂₄ still remain the top priorities to be addressed. To date, researchers have been focusing on the improvement of NCM electrochemical performance via synthesis of nanostructures, *i.e.*, nanoparticles [214], nanobricks [215-217], nanobars [88, 218], and porous or hollow spheres and hierarchical nano-/micro structures [100, 219, 220]. Substantial works reported so far demonstrated as nanostructuring can effectively enhance the rate capability via increasing the contact area with the electrolyte for charge transfer and, most important, shortening the length of the ionic transport path. In fact, the key and prerequisite to achieve the desirable electrochemical performance is to improve the Li⁺ transfer kinetics because the lithium ions diffusion ($\sim 10^{-11}$ cm² s⁻¹) is much more sluggish than charge transfer ($\sim 10^{-5}$ S cm⁻¹) [101].

Besides the synthesis of nanostructured materials, another efficient way to solve the problem of sluggish lithium ions diffusion is to increase the fraction of the electrochemical active facets (*i.e.*, {010} facets) [147, 221, 222]. NCM has the typical layered α -NaFeO₂ structure which provides two-dimensional tunnels for lithium ions diffusion along to *a* (or *b*) axis. The NiO₆, CoO₆ and MnO₆ octahedra perpendicular to the *c* axis form densely packed MO₂ layers (*i.e.*, {001} [223] planes), which prohibit the lithium ion diffusion along the *c* axis. Therefore, these 001 planes are considered as electrochemical inert planes, similarly to the basal planes of graphite. In contrary, the six-sided planes, namely (010), (0⁻ 10), (100), (⁻ 100), (1⁻ 10) and (⁻ 110), provide open structure for easy Li⁺ diffusion. However, maximizing the exposure of {010} electrochemical active facets while preventing the growth of crystal along the {001} poses a huge challenge because the unstable {010} facets, *i.e.*, having higher surface energy, have a tendency to disappear upon the crystal growth [222]. Therefore, many researchers focused on adding some surface-capping agent or chelating stabilizer to absorb onto the {001} planes in order to slow down the crystal growth rate, result in the higher exposure of {010} active

facets. As reported, polyvinylpyrrolidone (PVP) is frequently used as a surface-capping agent. Fu *et al.* successfully synthesized NCM₃₃₃ hexagonal nanobricks with exposure of {010} facets via the assistance of PVP using Ni_{1/3}Co_{1/3}Mn_{1/3}OH as precursor [217]. Li *et al.* reported NCM₃₃₃ nanoplates using ethylene glycol as the chelating stabilizer to expose more {010} facets [223]. However, for both of the above-mentioned studies, the usage of either PVP or ethylene glycol undoubtedly increased the material cost. Although many studies reported the successful synthesis of NCM₃₃₃, LiNi_{0.8}Co_{0.15}Al_{0.05}O₂, LiCoO₂ and Li_{1.2}Ni_{0.2}Mn_{0.6}O₂ with exposed {010} active facets, to the best of our knowledge, surfactant-free, 1D bar-like NCM₄₂₄ with preferentially exposed {010} facets has never been reported yet.

Herein, we report a facile surfactant-free synthesis route to successfully synthesize bar-like (1D) NCM₄₂₄ with preferentially exposed {010} electrochemical active facets using MC₂O₄·2H₂O (M=Li, Ni, Co, Mn) bars as precursor at room temperature. As it is shown later, the 1D bar-like, NCM₄₂₄ (marked as N-NCM) achieves remarkable electrochemical performance, especially at high C-rate and upon long-term cycling. The synergetic combination of the short (nano-sized) diffusion pathway for Li⁺ with the preferentially exposed {010} electrochemical active facets, greatly enhance the lithium ion transport kinetics, yielding excellent high rate capability and superior long-term cycling retention.

4.2 Results and Discussion

The monodisperse bar MC₂O₄·2H₂O (M=Li, Ni, Co, Mn), which served as the precursor, was firstly prepared via a precipitation process using oxalic acid as the precipitant. The obtained MC₂O₄·2H₂O shows monodisperse bar-like morphology (Figure 4.1a) with submicron-sized width (~400 nm) and micro-sized length (~3 μm). The XRD pattern in Figure 4.1b verifies that the precursor is a mixture of nickel, cobalt, manganese and lithium oxalates. In order to maintain the bar morphology upon the high temperature calcination

process, the calcination strategy was carefully designed according to the TGA result of $\text{MC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (Figure 4.1c). The $\text{MC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ precursor was first preheated at relatively low temperature (*i.e.*, 450 °C). As revealed by SEM images (Figure 4.1d) this sample well maintained the bar morphology at such temperature. Afterwards, the preheated precursor was subsequently calcined at various, but higher temperatures, *i.e.*, 750 °C, 800 °C, 850 °C and 900 °C, to form the final products marked as N-NCM-750, N-NCM-800, N-NCM-850 and N-NCM-900, respectively.

Figure 4.1 (a) SEM image, (b) XRD pattern, (c) TGA data of the bar-like (1D) $\text{MC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (M=Li, Ni, Co, Mn) precursor; (d) SEM images of the bar-like (1D) $\text{MC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (M=Li, Ni, Co, Mn) precursor after pre-heating at 450 °C.

The morphology of the N-NCM materials was firstly characterized by SEM. Figure 4.2 displays the morphologies of N-NCM-750 (Figures 4.2a and 4.2e), N-NCM-800 (Figures 4.2b and 4.2f), N-NCM-850 (Figures 4.2c and 4.2g) and N-NCM-900 (Figures 4.2d and 4.2h). It is clearly seen that all samples display a well-maintained bar-like morphology with the exception of

N-NCM-900, which shows broken nano-sized particles. At lower calcination temperature, N-NCM-750 maintains the morphology of $\text{MC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ precursor with similar length (*ca.*, $\sim 3 \mu\text{m}$) but a relatively rougher surface. In fact, due to the dehydration, decomposition of oxalate and loss of oxygen, the bars shrink and densify during calcination [224-226]. Therefore, the surface roughness of NCM is related to preferential reduction of energetically less stable surfaces, which disappear at higher temperature. The width of N-NCM-800 (*ca.*, $\sim 200 \text{ nm}$) broadens as a result of crystal growth along energetically favorable axis. This phenomenon becomes more prominent at 850°C with the lateral size of the bar reaching about 300 nm . At the highest temperature (900°C), however, the bar-like morphology tends to break into nano-sized particles with quite smooth surface due to continuous crystal growth. The crystal size at different temperatures will be discussed later with XRD refinement.

To gain more insight into the morphology as well as the structure of N-NCM, high-resolution transmission electron microscope (HRTEM) measurements were performed. Figures 4.3a-c shows the TEM and HRTEM images of N-NCM-800 at different magnifications. The 1D bar-like morphology is clearly displayed in Figures 4.3 (panels a and b, the latter is the magnified image of region in the former). Figure 4.3c depicts lattice fringes of the plane with a spacing of 0.475 nm obtained from Figure 4.3b (region B). This plane is assigned to the (003) planes of the NCM cathode materials, implying that the projected image planes are parallel to the c-axial direction (parallel to (100), (010), or (110) planes). This also indicates that the lateral plane belongs to the {010} active facet, which provides open structures for unimpeded Li^+ insertion and extraction. The clear lattice fringes as well as the FFT pattern (insert) demonstrate the highly single crystalline structure of N-NCM-800. In order to check the elemental composition, TEM EDS mappings were also performed. Figure 4.3d displays the TEM image of target region and the elemental mappings of O, Ni, Co, and Mn. The EDS mappings reveal that all the elements are uniformly distributed. The atomic ratio of the elements Ni,

Co, and Mn is approximately 4:2:4, which is well consistent with the designed, stoichiometric values (Figure 4.3e).

Figure 4.2 Typical SEM images of N-NCM obtained at different calcination temperatures: (a, e) 750 °C (N-NCM-750), (b, f) 800 °C (N-NCM-800), (c, g) 850 °C (N-NCM-850), (d, h) 900 °C (N-NCM-900).

Figure 4.3 (a-c) TEM and HRTEM images of N-NCM-800; (d) target TEM image and elemental EDS mapping of O, Ni, Co, Mn and all elements; (e) EDS spectrum and corresponding result of element compositions.

For the investigation of the valence states of nickel, cobalt and manganese, X-ray photoelectron spectroscopy (XPS) measurement was performed. All the spectra were calibrated using the binding energy of C 1s (284.6 eV) in XPS analysis. The survey scan spectrum (Figure 4.4a) validates the presence of Li, C, O, Ni, Co and Mn without any other impurities. The major peaks centred at 854.7, 779.9 and 642.2 eV as shown in Figures 4.4b-d, are corresponding to Ni^{2+} , Co^{3+} and Mn^{4+} , respectively.

Figure 4.4 X-ray photoelectron spectroscopy spectra (a) survey scan, (b) Ni 2p, (c) Co 2p and (d) Mn 2p of N-NCM-800.

In order to investigate the structure of the N-NCM materials calcined at different temperatures, XRD measurements were conducted (Figure 4.5). All the XRD patterns can be indexed as single phase hexagonal α -NaFeO₂ layered structure (space group R(-)3m) of NCM without any impurity. The splitting of (006)/(102) and (108)/(110) peaks becomes more distinct, however, with increased calcination temperature, indicating that the fraction of the well-ordered layered structure increased as well. Furthermore, the diffraction peaks become sharper and narrower at higher temperature, confirming the increased crystallinity. For further investigation of the N-NCM structure, XRD refinements were performed. The cell parameters are listed in Table 4.1. The values of c/a are all larger than 4.96, suggesting that all samples possess highly ordered layered structure [227]. For all the four samples, the intensity ratio of (003)/(104) is larger than 1.2, indicating low degree of cation mixing. The crystallite sizes are calculated to be about 46 nm (N-NCM-750), 57 nm (N-NCM-800), 102 nm (N-NCM-850) and 208 nm (N-NCM-900). This trend is

consistent with the above-presented SEM results. According to our previous study, grain size around 50-60 nm plays a crucial rule in enhancing rate and cycling performance [101].

Figure 4.5 XRD patterns of N-NCM obtained at different calcination temperatures: 750 °C (green line), 800 °C (blue line), 850 °C (red line), 900 °C (black line).

Table 4.1 Structural cell parameters of N-NCM-750, N-NCM-800, N-NCM-850, N-NCM-900.

Sample	Molar ratios of Li: Ni: Co: Mn				Stoichiometries
	Li	Ni	Co	Mn	
N-NCM-750	1.03	0.40	0.21	0.40	$\text{Li}_{1.03}\text{Ni}_{0.40}\text{Co}_{0.21}\text{Mn}_{0.40}\text{O}_2$
N-NCM-800	1.01	0.40	0.20	0.40	$\text{Li}_{1.01}\text{Ni}_{0.40}\text{Co}_{0.20}\text{Mn}_{0.40}\text{O}_2$
N-NCM-850	0.99	0.40	0.20	0.41	$\text{Li}_{0.99}\text{Ni}_{0.40}\text{Co}_{0.20}\text{Mn}_{0.41}\text{O}_2$
N-NCM-900	0.97	0.41	0.21	0.40	$\text{Li}_{0.97}\text{Ni}_{0.41}\text{Co}_{0.21}\text{Mn}_{0.40}\text{O}_2$

Table 4.2 Chemical composition, from ICP-AES analysis, of N-NCM-750, N-NCM-800, N-NCM-850, N-NCM-900.

sample	a(Å)	c(Å)	c/a	V (Å ³)	Crystal size (nm)	$I_{(003)}/I_{(104)}$
N-NCM-750	2.8685	14.2409	4.9646	101.5079	46.2	1.6233
N-NCM-800	2.8693	14.2481	4.9657	101.5853	56.8	1.6338

N-NCM-850	2.8709	14.2571	4.9661	101.7634	102.3	1.7256
N-NCM-900	2.8729	14.2685	4.9666	101.9862	207.9	2.0588

For the confirmation of the Li: Ni: Co: Mn composition, ICP-AES measurements were performed (Table 4.2). The results indicate that the as-obtained products to be $\text{Li}_{1.03}\text{Ni}_{0.40}\text{Co}_{0.21}\text{Mn}_{0.40}\text{O}_2$ (N-NCM-750), $\text{Li}_{1.01}\text{Ni}_{0.40}\text{Co}_{0.20}\text{Mn}_{0.40}\text{O}_2$ (N-NCM-800), $\text{Li}_{0.99}\text{Ni}_{0.40}\text{Co}_{0.20}\text{Mn}_{0.41}\text{O}_2$ (N-NCM-850) and $\text{Li}_{0.97}\text{Ni}_{0.41}\text{Co}_{0.21}\text{Mn}_{0.40}\text{O}_2$ (N-NCM-900). It is worth noting that the Li: Ni: Co: Mn ratio in all samples is quite consistent with the expected $\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$ stoichiometry (*i.e.*, within the experimental error). The slightly decreasing lithium content upon increasing calcination temperature owes to the more severe evaporation of lithium. This may result in a more relevant $\text{Ni}^{2+}/\text{Li}^{+}$ cation mixing and, thus, may lead to stronger capacity decay and even structural collapse. Therefore, the sample calcined at 800 °C with its ideal stoichiometry, well-maintained morphology and layered structure, low cation mixing, and optimal particle size, seems to be the optimum material.

Figure 4.6 Cyclic voltammetry characterization of the N-NCM-800 material. (a) The initial five consecutive cyclic voltammograms curves at a scan rate of 0.1 mV s⁻¹ in the voltage range 2.5–4.5 V; (b) Cyclic voltammetric profiles at various scan rates (0.1–1.5 mV s⁻¹); (c) Peak current density as a function of the square root of scan rate; (d) consecutive 50 cycles of cyclic voltammograms profiles at a scan rate of 0.1 mV s⁻¹ in the voltage range of 2.5–4.5 V.

In order to verify that our design strategy of bar with preferentially exposed {010} electrochemical active facets can significantly enhance the lithium transfer kinetics, cyclic voltammetry measurements were performed to investigate the apparent lithium diffusion coefficient. Figure 4.6a shows the initial five consecutive cyclic voltammetry curves of the N-NCM-800 electrode. The initial redox peaks at 3.86/3.71 V, with a 0.15 V peak separation, correspond to the Ni²⁺/Ni⁴⁺ redox processes. The peak separation further reduces to *ca.*, 0.08 V in the following cycles, suggesting very small electrode polarization and good reversibility of the N-NCM-800 material. In Figure 4.6b are reported the cyclic voltammetry cycles for the same material at different scan rates. Linear relationships are observed from the plots of peak current

intensity versus the square root of scan rate, as shown in Figure 4.6c. According to the Randles-Sevcik equation: $I_p = 2.68 \times 10^5 n^{3/2} A D^{1/2} C \omega^{1/2}$ Eq. 4.1 where I_p is the peak current intensity (A), n is the number of electrons per involved in the redox reactions, A is the electrode area (1.13 cm²), D is the apparent diffusion coefficient of lithium ions, C is the molar concentration of lithium ions in N-NCM (6.55×10⁻² mol cm⁻³) and ω is the scan rate (mV s⁻¹). The lithium ion apparent diffusion coefficients are calculated to be 1.98×10⁻⁸ and 5.04×10⁻⁹ cm² s⁻¹ for the delithiation and lithiation processes of N-NCM-800. Such values are approximately two orders faster than reported in literature [101], indicating ultrafast lithium insertion and extraction in the bar material. Therefore, the material is expected to own excellent rate capability. Figure 4.6d shows fifty consecutive CV cycles at 0.1 mV s⁻¹. Initially, the anodic peak shifts toward lower voltages, however, upon cycling, the peak intensity increases slightly, due to the activation of electrode. All the curves almost overlap with each other upon cycling, suggesting excellent reversibility upon repeated charge/discharge processes owing to the unique bar-like morphology with preferentially exposed {010} active facets facilitating the lithium transfer and diffusion kinetics.

Figure 4.7 Selected electrochemical impedance spectra of N-NCM-800.

Figure 4.7 displays the selected electrochemical impedance spectra upon 100 continuous charge/discharge cycles at 0.1 C. The nature of the impedance plots is typical of conventional LIBs, a depressed semicircle in high-middle frequency and followed by a sharp straight line in the low frequency region [228]. The R_e shown in the insert panel of equivalent series resistance (ESR) refers to the internal resistance, a combination of total resistance from electrolyte, electrodes, separator. The high-frequency semicircle is assigned to the resistance of the formation of SEI layer and the corresponding constant phase element. The middle-frequency ascribes to the charge transfer resistance and its relative capacitance. The straight line in the low-frequency region corresponds to the Warburg diffusion process. After the first charge-discharge, the diameter of semicircles in both high and medium region increased, which is due to the formation of SEI layer. Afterwards, the resistance values decreased gradually and got stabilized after ~30 cycles, which is due to the electrode activation as well as the enhanced electronic conductivity [229-231].

To validate the superior high-rate capability and long-term cycling stability indicated by the CV and EIS test results, the electrochemical performance of the materials was investigated by cycling coin-cells at various C-rates (from 0.1 C to 10 C; 5 cycles at each rate) in the 3.0-4.3 V voltage range. Figures 4.8a and b display the comparison of rate capability of all the four samples. The initial capacities of N-NCM-750, N-NCM-850 and N-NCM-900 are 162.0, 166.2 and 160.5 mAh g⁻¹ at 0.1 C, respectively, all substantially lower than that of N-NCM-800 (173.9 mAh g⁻¹). The difference in capacity becomes more apparent at higher current densities. For instance, at 1 C, the capacities of N-NCM-750, N-NCM-850 and N-NCM-900 are 140.1, 139.8 and 126.2 mAh g⁻¹, respectively, *i.e.*, substantially lower than that of N-NCM-800 (152.8 mAh g⁻¹). At 10 C, the capacity of the former materials dropped to 60% (N-NCM-750), 68% (N-NCM-850) and 52% N-NCM-900, that of N-NCM-800. For further comparison of the cycling ability, all four samples were subjected to 100 cycles at 10 C during which they showed 71% (N-NCM-750), 94% (N-NCM-800),

79% (N-NCM-850) and 91% (N-NCM-900) capacity retention (Figure 4.8c). All the samples exhibited extremely high coulombic efficiency near 100% (Figure 4.8d), indicating almost negligible irreversibility. However, the material calcined at 800 °C, *i.e.*, N-NCM-800, shows the best performance. As shown in Figure 4.8e, N-NCM-800 delivers initial charge and discharge specific capacities (at 0.05 C), as high as 196.8 and 180.2 mAh g⁻¹, respectively, with a high first cycle Coulombic efficiency (*ca.*, ~91.6%). In the following cycles at various C-rates the Coulombic efficiency approached 100% while the capacity was well retained, *i.e.*, 177.1 (0.1 C) 152.8 (1 C) 141.7 (2 C), 122.7 (5 C) and 104.2 (10 C) mAh g⁻¹. To further examine the cycling performance of N-NCM-800, a few cells were cycled at various current rates for 100 cycles (Figure 4.8f). The initial discharge capacities were 173.9 (0.1 C) and 116.5 (10 C) mAh g⁻¹. Even after 100 cycles, the discharge capacity at the various C-rate was well retained, *i.e.*, 158.1 (0.1 C) and 109.4 (10 C) mAh g⁻¹ with reversible capacity retention ratios as high as 91% and 94%, respectively. The electrochemical performance is excellent and quite superior to that reported in literature with NCM₄₂₄-based materials so far (Table 4.3), especially regarding to high C-rate capability and long-term cycling stability. This promising performance is attributed to the designed NCM structure (1D bars) with preferentially exposed {010} electrochemical active facets and nano-sized diffusion length for lithium ions.

Figure 4.8 Electrochemical characterization of the N-NCM electrodes as cathode material for lithium ion batteries: (a) and (b) cycling behaviour of N-NCM-750 (orange), N-NCM-800 (red), N-NCM-850 (blue), and N-NCM-900 (purple) at various current rates from 0.1 to 10 C; (c) cycling performance of N-NCM-750 (orange), N-NCM-800 (red), N-NCM-850 (blue), and N-NCM-900 (purple) at 10 C for 100 cycles and their corresponding (d) coulombic efficiencies; (e) selected charge/discharge profiles of N-NCM-800 at various current rates (0.1 C, 0.2 C, 0.5 C, 1 C, 2 C, 5 C and 10 C) in the voltage range of 3.0–4.3 V; (f) long-term cycling performance of N-NCM-800 at 0.1 C, 1 C and 10 C for 100 cycles.

Table 4.3 Comparison of electrochemical performance (capacity, rate capability and cycling stability) of the best performing NCM materials [178, 214, 232–237].

Reference	Voltage Range/ V	Specific Capacity/ mAh g ⁻¹	Rate Capability/ mAh g ⁻¹	Cycling Retention
NCM [232]	2.0–4.7 V	203 (0.05 C)	---	82% after 20 cycles at 0.05 C
NCM [233]	2.75–4.35 V	177 (0.2 C)	89 (3 C)	58% after 70 cycles at 1 C
Zr-doped NCM [234]	2.6–4.7 V	162 (0.2 C)	124 (2 C)	80% after 50 cycles at 0.2 C 69% after 50 cycles at 2 C

NCM [235]	2.0-4.4 V	165 (0.35 C)	70 (7 C)	90% after 50 cycles at 0.35 C
Bi ₂ O ₃ -coated NCM [236]	2.5-4.6 V	214 (0.1 C)	120 (3 C)	82% after 100 cycles at 0.1 C
Micro-ball NCM [237]	2.5-4.5 V	187 (0.1 C)	160 (2 C) 143 (5 C)	80% after 50 cycles at 5 C
NCM/SWCN T composites [214]	2.5-4.5 V	160 (0.1 C)	130 (5 C) 120 (10 C)	92% after 500 cycles at 5 C 91% after 500 cycles at 10 C
Li ₂ ZrO ₃ -coated NCM [178]	2.8-4.5 V	178 (0.075 C)	156 (1.5 C)	96.6% after 50 cycles at 0.3 C
THIS WORK	3.0-4.3 V	177 (0.1 C)	123 (5 C) 104 (10 C)	91% after 100 cycles at 0.1 C 94% after 100 cycles at 10 C

For further understanding of the superior high C-rate capability and long-term cycling stability, both SEM and TEM measurements of N-NCM-800 electrode after 100 cycles at 0.1 C were performed. The SEM images at different magnifications are shown in Figures 4.9a and b, which show well maintained bar-like morphology of N-NCM-800 sample. Some broken particles, however, are not due to the galvanostatic cycling but because of the strong press of electrodes before assembling cells. The TEM image (Figure 4.9c) also reveals the bar morphology with smooth surface. The HR-TEM image with very clear lattice fringes as well as its corresponding FFT pattern in Figure 4.9d indicate the quite intact hexagonal layered structure of N-NCM-800, suggesting the very well maintained structural integrity.

Figure 4.9 (a) and (b) SEM images, and (c) and (d) TEM images of the bar-like (1D) N-NCM-800.

4.3 Conclusions

In this work, we designed and successfully prepared via a surfactant-free synthesis, 1D bar-like NCM₄₂₄ (N-NCM) with preferentially exposed {010} electrochemical active facets, with the aim to fasten the lithium ion transport kinetics and thus greatly enhanced the electrochemical performance. The lithium ion apparent diffusion coefficient, evaluated by CV, reveals as N-NCM-800 endows with ultrafast Li⁺ insertion/extraction and excellent cycling reversibility. Consequently, the N-NCM-800 electrode exhibits excellent high rate capability. Specifically, N-NCM-800 delivers very high initial capacity (~177.1 mAh g⁻¹) and achieves capacity retention of 91% (0.1 C) and 94% (10 C) after 100 cycles. Even tested at higher C-rates, the N-NCM-800 can still deliver 152.8, 141.7, 122.7 and 104.2 mAh g⁻¹ at 1 C, 2 C, 5 C and 10 C rates, respectively. Such an excellent combination of high rate and long-term cycling performance makes N-NCM-800 a highly potential candidate for practical lithium-ion battery applications with faster charge/discharge ability and superior cycle lifetime. More importantly, the facile and versatile synthesis route is anticipated to be applicable to other cathode materials.

Chapter 5

MnPO₄-coated NCM₄₂₄ for Lithium Batteries with Outstanding Cycling Stability and Enhanced De-/lithiation Kinetics

In this chapter, we report the successful synthesis of MnPO₄-coated NCM₄₂₄ (MP-NCM) as lithium battery cathode material. The MnPO₄ coating acts as an ideal protective layer to physically prevent the contact between the NCM active material and the electrolyte, thus, successfully stabilizing the electrode/electrolyte interface and preventing detrimental side reactions. Additionally, the MnPO₄ coating enhances the lithium de-/intercalation kinetics in terms of the apparent lithium ion diffusion coefficient when carefully optimized regarding the overall coating content and thickness. As a result, MP-NCM-based electrodes reveal greatly enhanced C rate capability and cycling stability – even under exertive conditions like extended operational potential windows, elevated temperature, and higher active material mass loadings.

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5.1 Introduction

Layered LiNi_xCo_yMn_zO₂ (with $x + y + z = 1$), as a derivative of LiCoO₂, has been intensively investigated in recent years due to its higher capacity, lower cost, enhanced environmental benignity, and higher structural stability compared with LiCoO₂ [43, 107, 238, 239]. Among the various potential compositions, nickel-rich and cobalt-poor compounds are of great interest for large-scale applications like electric vehicles (EVs) due to their superior capacity and energy density. In particular, cobalt-poor cathodes are of great relevance for these large-scale applications with respect to the worldwide reserves – not mentioning the toxicity and concentrated geographic distribution of cobalt [240, 241]. However, to meet the high requirements for these applications, several issues remain to be addressed, including an insufficient cycling stability, poor rate capability, and relatively low thermal stability originating from the inevitable Li⁺/Ni²⁺ cation mixing and structural instability as well as detrimental side reactions at the electrode/electrolyte interface [32, 196]. The latter lead to a continuous increase of the interfacial charge transfer resistance and severe transition metal dissolution, especially at elevated temperatures and/or when elevating the anodic cut-off potential [242, 243]. These issues are becoming even more severe for an increasing Ni content, resulting in a worsened electrochemical performance and substantial safety issues, such as the thermal runaway of the cell [30, 191]. Accordingly, a medium nickel content accompanied by a reduced cobalt content like in NCM₄₂₄ appears presently as the ideal compromise with respect to energy density, cycling stability, and safety [83]. The detrimental side reactions at the electrode/electrolyte interface, however, remain as performance-limiting issue. To address these, protective particle coatings are considered most promising [244], including the utilization of metal oxides [245, 246], phosphates [140, 247], fluorides [248, 249], or lithium containing binary metal oxides [144, 184]. The application of such coatings commonly leads to improved cycling stabilities, rate capabilities, and,

in some cases, even enhanced thermal stabilities [122, 250]. In particular, the implementation of surface coatings like phosphates, which are essentially electrochemically active, provide a high structural stability, and suitable lithium-ion conductivity appears advantageous in this regard. With respect to safety, the most suitable coatings are cobalt and manganese phosphate, providing superior thermal stabilities compared to other phosphates like iron, nickel, or copper. Furthermore, a comparison of cobalt phosphate coatings and aluminium phosphate ones revealed suppressed nickel dissolution upon cycling [140]. Cobalt, however, is not only toxic and expensive, but moreover considered to be highly critical regarding its general abundance and geographic distribution [251]. For these reasons, MnPO₄ appears as a very powerful coating material due to its natural abundance and environmental benignity as well as its high structural and thermal stability [124, 252]. Considering recent results for cobalt phosphate coatings [195] the application of an amorphous nano-scaled MnPO₄ surface layer may, moreover, improve the charge transfer at the electrode/electrolyte interface and, thus, allow for an advanced rate capability of the resulting cathodes.

With this in mind, we present herein the synthesis and investigation of bar-shaped, MnPO₄-coated NCM₄₂₄ (MP-NCM), including the optimization of the coating layer thickness to obtain the best possible electrochemical performance in combination with common organic carbonate-based and ionic liquid-based electrolytes. The findings reveal that the successful realization of a continuous nano-coating of NCM with MnPO₄ provides substantial advantages regarding the apparent lithium-ion diffusion and cycling stability – in particular, at elevated temperatures as well as for extended operational potentials and elevated mass loadings – rendering MP-NCM as an ideal candidate for safer high-energy lithium and lithium-ion batteries.

5.2 Results and Discussion

5.2.1 Materials Characterization

The actual manganese phosphate coating content was determined by means of ICP-OES, revealing values close to the targeted ones, *i.e.*, about 0.65, 1.61, and 2.45 wt% for MP-NCM-1wt%, MP-NCM-2wt%, and MP-NCM-3wt%, respectively. For simplicity reasons, however, we will refer to the three samples by using the targeted values in the following. The investigation of the as-synthesized and MnPO₄-coated NCM samples with different MnPO₄ contents (given in wt%) was conducted via scanning electron spectroscopy (SEM). Figure 5.1 displays the morphologies of pristine NCM (Figures 5.1a₁ and 5.1a₂), MP-NCM-1wt% (Figures 5.1a₃ and 5.1a₄), MP-NCM-2wt% (Figures 5.1a₅ and 5.1a₆), and MP-NCM-3wt% (Figures 5.1a₇ and 5.1a₈). All samples, generally, reveal a bar-like morphology with a length of about 3 μm and a width of around 300 nm. Such elongated primary particle morphology is well suited for realizing spherical secondary particles, *e.g.*, via spray drying, as commonly employed in commercial lithium-ion batteries, allowing for high tapping density and, thus, volumetric energy density. Based on our previous study in chapter 4, these bar-shaped particles reveal preferentially electrochemically active {010} surface facets, providing an advanced rate capability by facilitated lithium ion de-/intercalation. A more detailed comparison of the SEM micrographs at higher magnification (Figures 5.1a₂, 5.1a₄, 5.1a₆, and 5.1a₈) shows that the surface of the pristine NCM bars is very smooth, while it is relatively rough for the coated samples and increasing in roughness for higher MnPO₄ contents. This observation is confirmed by the carrying out high resolution transmission electron microscopy (HRTEM; Figure 5.1b) on pristine NCM (Figures 5.1b₁ and 5.1b₂) and MP-NCM-2wt% (Figures 5.1b₃ and 5.1b₄) as example for the coated samples. This comparison clearly exhibits the formation of an amorphous surface layer with a thickness of *ca.*, 5 nm in case of MP-NCM-2wt% on the rather smooth NCM particles. Besides, the detection of the d₀₀₃ lattice fringe, shown in Figure 5.1b₂, with an interplanar spacing of 0.475 nm indicates the successful synthesis of layered NCM with a well crystallized structure, which is confirmed by means of X-ray

diffraction (XRD; Figure 5.1c). The recorded XRD patterns for pristine (black), MP-NCM-1wt% (red), MP-NCM-2wt% (blue), and MP-NCM-3wt% (green) are all in good agreement with the reference for the α -NaFeO₂ layered structure and essentially identical, corroborating that the coating process does not affect the crystallinity of the NCM active material. Besides, no additional reflections are observed for the MP-NCM samples, indicating that the coating layer remains amorphous or quasi-amorphous, which is consistent with the HRTEM analysis.

Figure 5.1 (a) Typical SEM micrographs of (a₁,a₂) NCM, (a₃,a₄) MP-NCM-1wt%, (a₅,a₆) MP-NCM-2wt%, and (a₇,a₈) MP-NCM-3wt% at different magnifications; (b) HRTEM micrographs of (b₁,b₂) NCM and (b₃,b₄) MP-NCM-2wt%; (c) XRD patterns of NCM (black), MP-NCM-1wt% (red), MP-NCM-2wt% (blue), and MP-NCM-3wt% (green).

To further confirm the formation of MnPO₄ on the particle surface, we complemented the SEM, HRTEM, and XRD analysis by X-ray photoelectron

spectroscopy (XPS; Figure 5.2). The survey scan for NCM and MP-NCM-2wt% (studied exemplarily for the coated samples) is presented in Figure 5.2a, evidencing the presence of Li, Ni, Co, Mn, and O in both samples. Both spectra were calibrated by means of the C1s peak of the adventitious carbon, centered at 284.8 eV (Figure 5.2b). As expected, the P2p peak, indicative for the presence of the MP coating layer, is present only for MP-NCM-2wt% (Figure 5.2c). The determined binding energy of 133.4 eV is characteristic for tetrahedral PO₄ [192], confirming the earlier proposed formation of MnPO₄. The peak position observed in the Ni2p spectra (Figure 5.2d) centered at 854.4 and 854.6 eV for NCM and MP-NCM-2wt%, respectively, evidences the divalent oxidation state of nickel in both samples, while the minor difference in binding energy is well within the experimental error. Similarly, the Co2p spectrum (Figure 5.2e) reveals essentially the same binding energy of cobalt in both samples with the maximum intensity at 780.0 eV (NCM) and 779.9 eV (MP-NCM-2wt%), indicating its trivalent oxidation state. Interestingly, the overall nickel and cobalt intensity is much lower for the coated sample, confirming the presence of a coating layer that does not comprise any nickel or cobalt with respect to the surface-sensitivity of the XPS technique. Differently, the Mn2p spectra (Figure 5.2f) show a comparable intensity as a result of the presence of manganese in the surface coating. The formation of MnPO₄ in addition to the presence of manganese in NCM is further evidenced by the slight shift from 842.3 eV (NCM) to 842.6 eV (MP-NCM-2wt%) due to the strong bonds between manganese and PO₄. In sum, these results – taking into account also the XRD, SEM, and HRTEM findings – confirm the successful formation of a uniform MnPO₄ coating layer on the as-synthesized NCM.

Figure 5.2 Comparative XPS analysis of NCM (black) and MP-NCM-2wt% (red): (a) survey scan; (b)-(f) detailed spectra for (b) C1s, (c) P2p, (d) Ni2p, (e) Co2p, and (f) Mn2p. The position of the C1s peak was used for the spectra calibration.

5.2.2 Cyclic Voltammetry and Apparent Lithium-Ion Diffusion

In order to investigate the impact of the MnPO₄ coating on the electrochemical characteristics, we subjected the electrodes comprising the four different samples in a first step to cyclic voltammetry (Figure 5.3). In a first step, we compare the first three cyclic sweeps, recorded with a sweep rate of 0.1 mV s⁻¹ (Figures 5.3a-d). All four samples reveal the characteristic redox peak couple within a voltage range of 3.7 to 4.0 V, indicating the oxidation of Ni²⁺ to Ni⁴⁺ and its subsequent reduction as a result of the reversible lithium ion de-/intercalation [219]. For the MP-coated samples, in particular MP-NCM-2wt% (Figure 5.3c) and MP-NCM-3wt% (Figure 5.3d), we observed, moreover, a redox peak couple of relatively low intensity at around 2.7-3.0 V (marked by a red frame), related to the redox activity of manganese (Mn³⁺/Mn⁴⁺) in the

MnPO₄ coating layer [121]. It is rather difficult to be detected for MP-NCM-1wt% - presumably due to the very low coating content – while it is more pronounced for MP-NCM-3wt% compared to MP-NCM-2wt% as a result of the relatively higher MP content. It is worth mentioning that this redox reaction is apparently reversible upon cycling, evidencing the stability of the coating layer structure. A more detailed analysis of the peak positions and the resulting peak separation is provided in Table 5.1. For as-synthesized NCM, for instance, the maximum intensity for the anodic and cathodic peak is recorded at 3.877 and 3.722 V, respectively, accounting for a peak separation of 0.155 V in the first cyclic sweep. This peak separation decreased to 0.1 V in the third cyclic sweep, indicating a decreasing polarization upon the initial de-/lithiation cycles. For MP-NCM-1wt% and MP-NCM-2wt% we determined even less peak separation for the first (0.1516 and 0.1186 V) and third (0.0970 and 0.0922 V) cyclic sweep, evidencing a beneficial effect of the MP coating for the lithium de-/intercalation kinetics. Contrarily, the MP-NCM-3wt% sample revealed a significantly higher polarization (0.2358 and 0.2699 V in the first and third cyclic sweep, respectively), suggesting that the coating layer has a detrimental effect, if the overall MP concentration is too high. For this reason, we did not continue with the investigation of MP-NCM-3wt%.

Table 5.1 Redox peak positions and the resulting peak separation obtained from the cyclic voltammetry study, presented in *Figures 5.3a-5.3d*.

	1 st Cycle		3 rd Cycle	
	Peak Position (anodic / cathodic) (V)	Peak Separation (V)	Peak Position (anodic / cathodic) (V)	Peak Separation (V)
NCM	3.8767 / 3.7219	0.1548	3.8218 / 3.7218	0.1000
MP-NCM-1wt%	3.8782 / 3.7266	0.1516	3.8318 / 3.7348	0.0970
MP-NCM-2wt%	3.8517 / 3.7331	0.1186	3.8214 / 3.7292	0.0922
MP-NCM-3wt%	3.9039 / 3.6681	0.2358	3.9200 / 3.6501	0.2699

Table 5.2 Calculated apparent lithium ion diffusion coefficients for the de-/lithiation of NCM, MP-NCM-1wt%, and MP-NCM-2wt% based on the data presented in *Figures 5.3e-5.3h*.

	Apparent Lithium Ion Diffusion Coefficient	
	Delithiation ($\text{cm}^2 \text{s}^{-1}$)	Lithiation ($\text{cm}^2 \text{s}^{-1}$)
NCM	1.85×10^{-8}	4.85×10^{-9}
MP-NCM-1wt%	2.24×10^{-8}	3.89×10^{-9}
MP-NCM-2wt%	3.28×10^{-8}	7.64×10^{-9}

The de-/lithiation kinetics were further investigated by subjecting the electrodes to steadily increasing sweep rates (Figures 5.3e to 5.3g). Generally, the three samples reveal the same trend, *i.e.*, an increasing evolving current and an increasing peak separation for elevated sweep rates. Determining the maximum current intensities and plotting it as a function of the square root of the applied scan rate allows for the calculation of the apparent lithium ion diffusion coefficient (Table 5.2) according to the Randles-Sevcik equation [90, 101]. Following these calculations, MP-NCM-2wt% shows the highest apparent lithium ion coefficients of 3.28×10^{-8} and $7.64 \times 10^{-9} \text{ cm}^2 \text{s}^{-1}$ for the delithiation and lithiation process, respectively. These values are almost twice as high as for as-synthesized NCM and MP-NCM-1wt%, confirming that the coating layer does not have a detrimental effect on the lithium de-/intercalation kinetics, if the MP content is well adjusted.

Figure 5.3 Cyclic voltammetry: (a)-(d) The initial three cyclic sweeps at a scan rate of 0.1 mV s⁻¹ in the voltage range of 2.5-4.5 V vs. Li/Li⁺, *i.e.*, (a) NCM, (b) MP-NCM-1wt%, (c) MP-NCM-2wt%, and (d) MP-NCM-

3wt%. (e)-(h) The subsequent cyclic sweeps at increasing scan rates in the range from 0.1 up to 1.5 mV s⁻¹ for (e) NCM, (f) MP-NCM-1wt%, and (g) MP-NCM-2wt%. Panel (h) reports the linear response of the peak current intensity as a function of the square root of the increasing scan rate to determine the apparent lithium ion diffusion coefficient (see Supporting Information for more details).

Figure 5.4 Galvanostatic cycling (a) of electrodes based on NCM, MP-NCM-1wt%, and MP-NCM-2wt% at varying C rates, followed by constant current cycling at 1C; (b) Constant current cycling at 0.1C of electrodes comprising NCM or MP-NCM-2wt% as active material; (c) Constant current cycling of MP-NCM-2wt%-based electrodes at 1C, 2C, and 10C after three formation cycles at 0.1C (voltage range: 3.0 to 4.3 V vs. Li/Li⁺).

5.2.3 Galvanostatic Cycling and Rate Capability

To further confirm the advantageous impact of the MP coating on the de-/lithiation kinetics, we subjected the electrodes comprising NCM, MP-NCM-1wt%, and MP-NCM-2wt% to galvanostatic cycling at elevated dis-/charge rates, varying the C rate from 0.1C to 10C, and subsequently constant current cycling for additional 100 cycles at 1C (Figure 5.4a). At relatively low rates of 0.1C, the obtained specific capacity is slightly lower for the coated samples,

following the order NCM (166.2 mAh g⁻¹) > MP-NCM-1wt% (162.2 mAh g⁻¹) > MP-NCM-2wt% (158.2 mAh g⁻¹), due to the inactivity of the MnPO₄ coating in this potential range of 3.0 to 4.3 V vs. Li/Li⁺. For increasing C rates, however, the specific capacities are higher for the coated samples compared to as-synthesized NCM. Eventually, it leads to a reversed order regarding the obtained capacity, *i.e.*, MP-NCM-2wt% (101.5 mAh g⁻¹) > MP-NCM-1wt% (92.0 mAh g⁻¹) > NCM (70.5 mAh g⁻¹) at 10C. Moreover, the capacity retention for the subsequent 100 cycles at 1C is greatly improved by applying the MP coating, allowing for capacity retentions of 96.7% and 93.7% for 2 wt% and 1 wt% of MP, respectively, compared to only 80.6% for as-synthesized NCM. In Figure 5.4b, we compare the cycling stability at 0.1C constant current cycling, revealing a capacity retention of 89.7% for as-synthesized NCM, which is significantly lower as for the two coated samples, providing a capacity retention of 94.6% in case of MP-NCM-1wt% and 95.6% in case of MP-NCM-2wt%. Once more, the as-synthesized sample shows the highest initial capacity at such low C rates, but the worst capacity retention in comparison with the coated samples, while 2 wt% of MP appear ideal for optimizing the electrochemical performance. We may assume at this point that the enhanced performance is a result of the improved de-/lithiation kinetics in combination with a stabilized electrode/electrolyte interface, preventing, *e.g.*, the dissolution of transition metals into the electrolyte upon cycling. While an MP coating content of 1 wt% reveals already a substantial improvement, the beneficial effect of the MP surface layer is even more pronounced for a slightly higher MP content of 2 wt%. Consequently, we focused on MP-NCM-2wt% for the following studies. To complete the investigation of the capacity retention as a function of C rates, we subjected these electrodes also to 100 cycles constant current cycling at 1C (without a C rate test beforehand), 2C, and 10C (Figure 5.4c). As expected, the capacity retention is higher for increasing C rates – *i.e.*, 95.6%, 96.0%, 99.2%, and 102.7% for 0.1C, 1C, 2C, and 10C, respectively – which indicates that the capacity loss is largely resulting from interfacial reactions at elevated potentials,

since the electrode is exposed to higher potentials for much longer time in case of lower C rates. The value of 102.7% is apparently resulting from a slight initial capacity increase, presumably due to some activation process(-es), when applying such high dis-/charge rates right after the three formation cycles at 0.1C. Selected corresponding potential profiles (in comparison with those for as-synthesized NCM at C rates of 0.1C, 2C, and 10C) are presented in Figure 5.5. The electrodes based on MP-NCM-2wt% reveal a substantially reduced polarization as a function of constant current cycling at elevated C rates of 2C and 10C compared to NCM and, accordingly, greatly enhanced capacity retention. Remarkably, the capacity retention is the highest at 0.1C for as-synthesized NCM (*i.e.*, 89.7%) compared to 78.2% and 78.9% at 2C and 10C, respectively, suggesting that the dramatically improved rate capability in case of MP-NCM-2wt% is mainly related to the higher de-/lithiation kinetics rather than detrimental side reactions at such elevated C rates. The detailed summarizing comparison of the obtained discharge capacities for these two samples is provided in Table 5.3.

5.2.4 Galvanostatic Cycling under Exertive Conditions

To further stress the beneficial effect of the MnPO₄ coating, we conducted a series of experiments at more exertive conditions by (a) extending the operational potential window, (b) conducting galvanostatic at elevated temperature, and (c) increasing the active material mass loading (Figure 5.6). The results are discussed in the following three paragraphs.

a) Extending the Operational Potential Window

In a first step, we increased stepwise the anodic cut-off potential from 4.3 to 4.4 and eventually to 4.5 V (selected dis-/charge profiles are shown in Figures 5.6a, 5.6b, and 5.6c, respectively), while keeping the cathodic cut-off potential constant at 3.0 V. An elevated charge cut-off potential of 4.4 and 4.5 V lead to increased discharge capacities of 115.6 and 129.2 mAh g⁻¹, respectively, compared to 107.5 mAh g⁻¹ at 10C, which is expected as more

lithium ions are deintercalated when raising the anodic cut-off potential and subsequently re-intercalated. The capacity retention remains high after 100 cycles for 4.4 V (98.1%), but slightly deteriorates for an even higher cut-off potential of 4.5 V, indicating that a value of either 4.3 or 4.4 V is optimal with respect to long-term cycling at such elevated C rates.

Figure 5.5 Comparison of selected dis-/charge profiles for (a-c) NCM and (d-f) MP-NCM-2wt% at varying C rates, *i.e.*, (a,d) 0.1C, (b,e) 2C, and (c,f) 10C. The corresponding ‘capacity vs. cycle number’ plots are presented in Figure 5.4 for MP-NCM-2wt%.

Table 5.3 Summarizing comparison of the obtained discharge capacities at different C rates for NCM and MP-NCM-2wt% based on the dis-/charge profiles presented in Figure 5.5.

		NCM	MP-NCM-2wt%
1st Cycle / mAh g⁻¹	0.1C	165.4	159.6
	2C	139.1	133.4
	10C	108.8	109.1
10th Cycle / mAh g⁻¹	0.1C	162.7	158.9
	2C	136.6	134.6
	10C	107.8	111.6
20th Cycle / mAh g⁻¹	0.1C	159.6	157.9
	2C	132.6	134.3
	10C	104.6	111.3
50th Cycle / mAh g⁻¹	0.1C	154.6	155.4
	2C	122.0	133.3
	10C	97.8	111.1
100th Cycle / mAh g⁻¹	0.1C	148.4	152.6
	2C	108.2	131.6
	10C	85.7	110.5

In a second step, we extended also the discharge cut-off potential, lowering it from 3.0 to 2.5 V. The corresponding comparison of MP-NCM-2wt% and as-synthesized NCM is presented in Figures 5.6d and 5.6e, respectively. The electrodes were subjected to galvanostatic cycling at 0.1C for 100 cycles. While MP-NCM-2wt% reveals the characteristic feature for the manganese redox activity (Mn³⁺/Mn⁴⁺) as a result of the applied MnPO₄ coating at around 2.7 to 3.0 V upon discharge and charge – which is in good agreement with the findings reported in Figure 5.3. It is worthy to mention that the capacity retention is substantially improved for the coated sample, also under these

conditions, *i.e.*, it is 93.9% in case of MP-NCM-2wt% and only 84.6% in case of as-synthesized NCM.

Figure 5.6 Galvanostatic cycling under exertive conditions: (a)-(c) Selected dis-/charge profiles of MP-NCM-2wt%-based electrodes cycled at 10C for 100 cycles and setting the upper cut-off potential to (a) 4.3 V, (b) 4.4 V, and (c) 4.5 V, while keeping the lower cut-off potential constant at 3.0 V; Comparison of selected dis-/charge profiles for electrodes based on (d) MP-NCM-2wt% and (e) as-synthesized NCM, subjected to 100 cycles at 0.1C, when lowering the cathodic cut-off potential to 2.5 V, while fixing the anodic cut-off to 4.3 V; (f) Galvanostatic cycling at an elevated temperature of 60 °C in comparison with electrodes based on as-synthesized NCM (100 cycles at 10C after three formation cycles at 0.1C); (g)-(i) Impact of increasing the active material mass loading to about 4 and 6 mg cm⁻²: (g) rate capability and subsequent cycling at 1C for 100 cycles; constant current cycling at (h) 2C and (i) 10C after three formation cycles at 0.1C (3.0 to 4.3 V vs. Li/Li⁺).

b) Galvanostatic Cycling at Elevated Temperature

For the evaluation of the cycling stability at elevated temperature, we subjected electrodes based on NCM and MP-NCM-2wt% to 100 galvanostatic cycles at 10C and increased the ambient temperature to 60 °C (Figure 5.6f), which is considered as very harsh conditions with respect to the reactivity of the organic carbonate-based electrolyte containing LiPF₆ as conducting salt. As expected, the initial capacity increased slightly for both samples, while it was still higher for as-synthesized NCM (173.1 mAh g⁻¹) compared to the coated sample (166.6 mAh g⁻¹), in accordance with the previous findings. However, the capacity continuously faded for as-synthesized NCM, while it remained stable for the MnPO₄-coated NCM, resulting in superior capacity retention for the latter of 97.3% compared to 85.7%. Considering the commercial application of these active materials as lithium battery cathodes, this advanced cycling stability even at temperatures as high as 60 °C is of great importance, thus further highlighting the advantageous impact of such a coating.

We may note that the increase in capacity for elevated C rates becomes more pronounced compared to the relatively lower C rates (*e.g.*, 0.1C), which is assigned to the enhanced ionic conductivity of the electrolyte at elevated temperature [253] and the increased interlayer spacing within the cathode, *i.e.*, the enhanced lithium diffusion within the layered structure [254]. This effect is, apparently, crucial when the electrode is subjected only to rather short dis-/charging times, *i.e.*, high C rates.

c) Increasing the Active Material Mass Loading

In the context of a potential commercial application, we studied in a subsequent step the effect of increasing the active material mass loading to about 4 and 6 mg cm⁻². These values are still lower than those realized in commercial high-energy lithium-ion batteries, but comparably high considering that the electrode preparation process has not yet been optimized in this regard.

The results for the different C rates studied herein are presented in Figure 5.6g (C rate test and subsequent constant current cycling at 1C), Figure 5.6h (constant current cycling at 2C), and Figure 5.6i (constant current cycling at 10C). For relatively low C rates, *i.e.*, up to 2C, basically no difference is observed and all electrodes reveal stable cycling and good capacity retention (Figures 5.6g and 5.6h). At higher C rates, *i.e.*, 5C and 10 C, the electrodes having elevated mass loadings provide slightly lower discharge capacities, though still exceeding 110 and 80 mAh g⁻¹ at 5C and 10C, respectively (Figure 5.6g). When subjecting the electrodes to an extended cycling at 10C, however, the capacity is slightly fading for a mass loading of about 4 mg cm⁻² and a more pronounced fading is observed for those electrodes having a mass loading of around 6 mg cm⁻². Nevertheless, even in the latter case, the electrodes provide a capacity retention of 78.5% after 100 cycles at 10C (compared to 90.8% in case of 4 mg cm⁻²).

5.2.5 *Ex situ TEM Analysis*

To eventually investigate the impact of the MP coating on the improved electrochemical performance and, particularly, the cycling stability, we conducted an *ex situ* TEM analysis of electrodes based on MP-NCM-2wt% and as-synthesized NCM after 100 constant current cycles at 0.1C (employing the standard organic carbonate-based electrolyte). The results are depicted in Figure 5.7. Compared with the pristine material (Figure 5.1b), the cycled MP-NCM-2wt% reveals a slightly roughened surface (Figures 5.7a and 5.7b), which is presumably linked to oxidative electrolyte decomposition reactions and other aging mechanisms, commonly occurring in a lithium battery upon extended cycling [255]. However, these changes are only apparent when looking at higher magnifications (Figure 5.7b), while at lower magnifications (Figure 5.7a) the general particle morphology appears to be well maintained. In fact, the Fast Fourier Transform (FFT) pattern, shown as inset in Figure 5.7b, reveals a highly crystalline structure even after such extended cycling. Contrarily, the as-

synthesized NCM presents substantial aging even at lower magnifications (Figure 5.7c) and a very rough particle surface – presumably as a result of dramatic side reactions upon the 100 cycles at rather low C rate, subjecting the electrode for relatively long times to elevated potentials. The surface of the micro-sized NCM particles (Figure 5.7d) is constructed of many nanocrystalline particles, as also reflected in the rather diffuse FFT pattern, shown in the inset, revealing several polycrystalline rings.

Accordingly, the realization of a uniform, but thin MnPO₄ coating layer can effectively prevent the substantial aging mechanisms occurring for the as-synthesized NCM particles, presumably including inter alia transition metal dissolution and HF etching, thus, allowing for greatly stabilized electrode/electrolyte interfaces and an enhanced structural stability at the particle surface.

Figure 5.7 TEM micrographs of (a,b) MP-NCM-2wt% and (c,d) as-synthesized NCM at different magnifications after 100 cycles at 0.1C employing the standard organic carbonate-based electrolyte; in the inset of (b) and (d) corresponding FFT patterns are provided.

5.3 Conclusions

We successfully synthesized MnPO₄-coated NCM₄₂₄ (MP-NCM) with different coating contents, out of which an overall MnPO₄ concentration of 2 wt% appeared most effective in enhancing the lithium cycling stability and de-/intercalation kinetics. The latter result in an improved rate capability compared to as-synthesized NCM, while the former allows for superior capacity retentions – independent of the applied dis-/charge rate. Moreover, the application of such MnPO₄ coating leads to substantially enhanced cycling stabilities even under exertive conditions like extended operational potential windows (charge and discharge), elevated temperatures as high as 60 °C, and increased active material mass loadings. This improved electrochemical performance is assigned to a remarkably stabilized electrode/electrolyte interface, as the MnPO₄ coating layer effectively prevents detrimental side reactions with the electrolyte and the aging of the active material upon cycling by preserving a relatively smooth particle surface and structural integrity.

We may anticipate that this strategy can be readily employed also for other state-of-the-art and next generation cathode materials with greatly extended de-/lithiation kinetics and advanced cycling stabilities – even under exertive conditions.

Chapter 6

Long-life Full Lithium (-ion) Cells with High Energy and Power Densities, Incorporating MnPO_4 -coated NCM_{424} as Cathode Material

In this paper, a high-performance lithium-ion full cell via combining commercial SLP 30 graphite as anode and $\text{MnPO}_4@\text{NCM}_{424}$ (MP-NCM) as cathode material is proposed. This battery shows remarkable long-term cycling stability over 2000 cycles at 1 C, sustaining capacity retention ratio up to 74.1% with high average Coulombic efficiency of ~99.96%. Furthermore, the cell achieves a maximum gravimetric energy density and power density estimated as 376.2 Wh kg^{-1} and 1.8 kW kg^{-1} (refer to the total active material weight, i.e., SLP 30 graphite + MP-NCM). The system studied here is expected to give a feasible guidance for the fabrication and manufacture of high performance lithium-ion batteries for future practical applications. Employing an ionic liquid as alternative, intrinsically safer electrolyte system allows for outstanding cycling stabilities with a capacity retention of well above 85% after 2000 cycles, rendering this approach highly promising also for other state-of-the-art and next generation lithium battery cathodes.

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6.1 Introduction

According to our previous studies (Chapter 5), we have successfully repressed the side reactions via coating an amorphous layer of MnPO_4 on the surface of NCM_{424} (denote as MP-NCM onwards). Although the initial capacity showed a slightly decrease after coating, the high C-rate capability and long-term cycling stability were significantly enhanced, even when tested at some abuse conditions (*ca.*, over charge, over discharge, elevated temperature, high mass loadings).

With respect to the anode side, graphite, which delivers *ca.*, 372 mAh g^{-1} capacity with good cycling stability, is the most commonly used anode material. The property of low negative potential of lithium de-/intercalation makes it particularly attractive in practical applications [256, 257]. Therefore, in this chapter, we report a high-performance lithium-ion full cell wherein SLP 30 graphite is employed as anode material and $\text{MnPO}_4@ \text{NCM}_{424}$ (MP-NCM) is employed as cathode material (denote as graphite/MP-NCM hereafter). The morphology and structure of SLP 30 graphite and MP-NCM were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and powder X-ray diffraction (PXRD). The manganese phosphate coated cathode material plays a decisive role in achieving such a remarkable electrochemical performance. In detail, when applied as full lithium-ion cell in three electrodes configuration, the batteries achieved high capacity, good rate capability, stable cycling stability upon 2000 cycles at 1 C rate with very high energy density and power density.

As the anode, metallic lithium possesses outstanding energy density (3862 mAh g^{-1}), volumetric density (2047 Ah L^{-1}), and the most electropositive potential among all metals (theoretically -3.04 V vs. SHE) [258]. However, the utilize of conventional liquid alkaline organic electrolyte, which is highly volatile, flammable and toxic, has ruled out the potential of using lithium metal as anode because of their poor compatibility, leading to dendrite formation upon charge [259]. Therefore, in a next step, we replaced the standard organic

carbonate-based electrolyte with a non-flammable, non-volatile ionic liquid-based one (0.2LiTFSI-0.8PYR₁₄FSI) [260]. Due to the good compatibility between ionic liquid and metallic lithium, thus, it allows the use of lithium metal as anode and may lead to lithium batteries with higher safety and energy performance compared with the currently available LIBs. Therefore, in this chapter, we also assembled full lithium cells incorporating an ionic liquid-based electrolyte allows for outstanding cycling stabilities, contributing to the ongoing success of lithium-based batteries for such important applications as electric vehicles.

6.2 Results and Discussion

6.2.1 Characterizations of SLP 30 Graphite

The morphology of SLP 30 graphite was analyzed by SEM as shown in Figure 6.1a, wherein SLP 30 graphite displays ‘potato-shaped’ morphology with an average particle size around 32 μm . Figure 6.1b shows the XRD pattern of SLP 30. The peaks located at 26.5°, 44.3°, and 54.5° correspond to (002), (101), and (004) planes (Figure 6.1b inset), respectively. The sharp intensity of peaks (002) indicates that the SLP 30 is highly crystallized.

Figure 6.1 (a) SEM image and (b) XRD pattern of SLP 30 graphite.

6.2.2 Electrochemical Performance of SLP 30 Graphite

In order to test the cycling stability, the SLP 30 graphite electrode was subjected to 200 cycles at 1 C rate in the voltage range of 0.02–1.5 V (Figure 6.2). The first cycle was measured at a lower C-rate, *ca.*, 0.05 C, for the activation of the material to form uniform and stable solid electrolyte interface (SEI) layer on the surface. When jumped to 1 C rate, the SLP 30 graphite electrode achieved 357.2 mAh g⁻¹ capacity with a high Coulombic efficiency of 98.6%. After ~ 20 cycles of continuous electrode activation, the SLP 30 electrode reached a stable status with high reversible capacity, *ca.*, 380 mAh g⁻¹. Meanwhile, the Coulombic efficiency approached to 99.8%, indicating the cell was operated with a high efficiency, hence, a long cycling life is expected. After 200 cycles, still, ~338.2 mAh g⁻¹ capacity was delivered, maintaining a capacity retention ratio of 94.7% of initial capacity.

Figure 6.2 Cycling performance of SLP 30 graphite at 1 C over 200 cycles.

6.2.3 Electrochemical Behavior of SLP 30 Graphite and MP-NCM in Half Cell Configuration

Figure 6.3a displays the initial five consecutive cyclic voltammetry profiles of graphite/Li (green) and MP-NCM/Li (black) in half cells for the purpose of investigating their electrochemical behaviors. The redox peaks of graphite/Li correspond to lithium-ion de-/intercalation into/from the graphite. It is notable that there's an increase in redox currents upon successive cycling, indicating that the graphite is slowly being 'conditioned' [257]. Therefore, the

active material utilization is increased, which is in consistent with the cycling performance shown above. A small peak centered at ~ 0.7 V, which is due to SEI film formed on the surface of graphite [261], occurred during the first cathodic scan. Before the intercalation of lithium ions into the graphite, there's a reductive decomposition of electrolyte solvents and hence a thin electrically insulating but ionically conductive film is formed [257]. This SEI layer prevents the active material from further contact with the electrolyte, and acts like a barrier for solvated lithium ions, only allowing charge carriers without a solvation sphere to enter the graphite structure. The anodic/cathodic peaks located at $\sim 3.82/3.72$ V is attributed to the redox couple of $\text{Ni}^{2+} \leftrightarrow \text{Ni}^{3+} \leftrightarrow \text{Ni}^{4+}$ [101]. The symmetry of the CV peaks indicates good reversibility with small polarization during the dis-/charge process within the sample. The small redox peaks between 2.5–3.0 V, although not very obvious, are due to the redox reaction of $\text{Mn}^{3+}/\text{Mn}^{4+}$ of MnPO_4 coating layer. The steady state dis-/charge profiles of SLP 30 graphite (green) and MP-NCM (black) in lithium half cells are shown in Figure 6.3b. As expected, typical solid-solution like behavior is observed from the de-/lithiation profile of MP-NCM, with a capacity of 158 mAh g^{-1} delivered. With respect to that of SLP 30 graphite, three stages related to lithium-ion intercalation/de-intercalation were clearly seen, *ca.*, 0.2 V, 0.11 V and 0.07 V. The capacity approached to theoretical capacity $\sim 370 \text{ mAh g}^{-1}$.

Figure 6.3 (a) Cyclic voltammetry profiles and a stable state charge/discharge profiles (0.1 C) of SLP 30 graphite (green) and MP-NCM (black).

6.2.4 Electrochemical Performance of SLP 30 Graphite/MP-NCM in Full Lithium-ion Cell Configuration

As supported by the electrochemical behavior and performance of both SLP 30 graphite and MP-NCM electrodes in half cells, the combination of SLP 30 graphite as anode and MP-NCM as cathode in a full cell configuration is expected to yield high rate performance and cycling stability. Hereby, we decided to prepare the cathode-limited SLP 30 graphite/MP-NCM full cells. The higher discharge capacity of SLP 30 graphite ensures a low working potential and thus the fully usage of cathode side. According to the above results, the specific capacity ratio of anode/cathode is calculated to be around 1 to 2.3 at 0.1 C. In order to well balance both anode and cathode sides, we carefully prepared SLP 30 graphite and MP-NCM electrodes, with mass loadings of $\sim 3.2 \pm 0.2$ and 6.2 ± 0.2 mg cm⁻², respectively. The weight ratio of SLP 30 graphite: MP-NCM is between 1.77–2.13. Therefore, the capacity ratio of anode/cathode ranges from 1.09 to 1.31. The differential capacity plot is shown in Figure 6.4a wherein three redox peaks centered at 3.51/3.53 V, 3.65/3.69 V, 3.89/3.91 V are observed. Figure 6.4c displays the initial four consecutive dis-/charge profiles of graphite/MP-NCM full cell in galvanostatic condition. The specific capacity delivered was calculated on the basis of cathode material mass loading. In order to activate the electrodes, the first cycle was tested at 0.05 C rate in the voltage range of 2.7–4.2 V, delivering initial dis-/charge capacities of 173.7/151.7 mAh g⁻¹ with an initial Coulombic efficiency of 87.3%. When increasing the current density to 0.1 C, still, the cell was capable of delivering 150.4 mAh g⁻¹ capacity with remarkable reversibility. Owing to the combination of graphite and MP-NCM, three clear stages upon charging were observed, *ca.*, 3.52–3.66 V, 3.66–3.88 V and 3.88–4.2 V, respectively. Accordingly, three stages, *ca.*, 4.2–3.84 V, 3.84–3.62 V, 3.62–3.46 V, occurred during the discharge process, which is consistent with the

result of three redox peaks demonstrated in Figure 6.4a. Figure 6.4b illustrates the typical dis-/charge profile with almost ideal symmetry of individual SLP 30 graphite (black dash line), MP-NCM (green dash line) and graphite/MP-NCM full cell (green solid line). By the comparison of the full cell profile and cathode side profile, it is notable that almost full usage of MP-NCM capacity is made. In order to test the rate capability of the full cell, we cycled the cells up to 5 C in galvanostatic and potentiostatic (CCCV) testing mode, after the initial cycle at low C-rate (0.05 C) for activation. Even at higher C-rates, the cell still achieved a capacity of 142.0, 132.0, 114.4 mAh g⁻¹ at 1 C, 2 C and 5 C (Figure 6.4d), respectively. These values compete well with those already reported in literature for lithium-ion batteries with advanced configuration [262, 263], due to the high C-rate performance of MP-NCM. Figure 6.4e reveals the cycling performance of the full cell. After initial few cycles at 0.1 C for activation, the cell was cycled at 1 C with 147.5 mAh g⁻¹ of capacity delivered. The capacity fading was stronger in the beginning 200 cycles. Afterwards, a relatively stable cycling performance was achieved. After 2000 cycles at 1 C, the cell achieved 74.1% of initial capacity with a capacity of 109.2 mAh g⁻¹ remained in the end, suggesting only an average capacity loss of 0.019 mAh g⁻¹ per cycle. After 1189 cycles, the cell reached the end of life criteria for usage in automotive applicants [255], with a capacity of 117.98 mAh g⁻¹ delivered.

Figure 6.4 (a) Differential capacity (dQ/dV) versus voltage plot of initial four charge/discharge profiles; (b) typical charge/discharge profile (0.1 C) of individual electrode: SLP 30 graphite (black dash line), graphite/MP-NCM (green solid line) and MP-NCM (green dash line); (c) initial four charge/discharge profiles; (d) rate performance in the range of 0.05-5 C, and (e) cycling performance at 1 C over 2000 cycles of graphite/MP-NCM full cell.

Ragone plots of various full cell configurations are shown in Figure 6.5 for comparison [256, 264-267]. The gravimetric energy density and power density of graphite/MP-NCM were calculated based on the total mass of active material (graphite and MP-NCM). From the datum displayed in Figure 6.5, a maximum gravimetric energy density of 376 Wh kg^{-1} at a delivered power density of 19.0 W kg^{-1} was achieved. When compared with other full cell systems, our cell shows substantially higher energy density with less loss at higher C-rates. Table 6.1 summarized the electrochemical performance of more full cell systems

reported so far. Although our cell shows relatively lower power density, still, a power density reached to over 1800 W kg^{-1} with energy delivered of 262 Wh kg^{-1} . Through comparison, to the best of our knowledge, our full cell exhibits the highest energy density with a remarkable cycling life up to 2000 cycles at 1 C.

Figure 6.5 Ragone plot displaying the gravimetric energy density and power density of graphite/MP-NCM full cell and other references.

Table 6.1 Electrochemical performance comparison with other full cell systems reported.

Full cell		Maximum	Maximum power	Total weight	Capacity
Cathode	Anode	energy density	density	used for	retention
		(Wh kg^{-1})	(W kg^{-1})	calculation	
LiFePO ₄ -CNT [264]	ZnFe ₂ O ₄ -C	202	3720	Based on active materials	85% after 1000 cycles at 10 C
LiFePO ₄ -KB	Li ₄ Ti ₅ O ₁₂	286	2492	Based on	88% after

[265]				limiting electrode	1300 cycles at 0.5 C
LiMn ₂ O ₄	Li ₄ Ti ₅ O ₁₂ -C	140	6880	Based on active materials	81% after 500 cycles at 1 C
[266]					
LiNi _{0.6} Co _{0.2} Mn _{0.2} O ₂ [267]	graphite	186	---	Based on electrodes, separator and current collector	---
AC+LiNi _{0.5} Co _{0.2} Mn _{0.3} O ₂	graphite	36.2	3910	Based on full cell weight	95% after 1000 cycles at 1 C
[256]					
LiNi _{0.45} Co _{0.01} Mn _{1.45} O ₄	Li ₄ Ti ₅ O ₁₂	372	---	Based on active materials	85.4% after 500 cycles at 1 C
[268]					
Li _{1.2} Ni _{0.4/3} Co _{0.4/3} Mn _{1.6/3} O ₂	Sn-C	220	---	Based on full cell weight	75% after 500 cycles at 100 mA g ⁻¹
[269]					
xLi ₂ MnO ₃ •(1-x)LiMn _{0.4} Ni _{0.4} Co _{0.2} O ₂	Hard carbon	315	---	Based on active materials	84% after 50 cycles at C/11
[270]					
0.5Li ₂ MnO ₃ •0.5LiMn _{0.5} Ni _{0.5} O ₂ [271]	Mn _x Co _{1-x} O ₂	360	---	Based on active materials	95.8% after 130 cycles at 0.2 C
[271]					
0.5Li ₂ MnO ₃ •0.5LiMn _{0.4} Co _{0.2} Ni _{0.4} O ₂	Li ₄ Ti ₅ O ₁₂	205	---	Based on active materials	97% after 250 cycles at 1C

[272]						
MnPO ₄	graphite	376	1841	Based on	81.6% after	
coated				active	1000 cycles	
LiNi _{0.4} Co _{0.2} M				materials	at 1 C	
n _{0.4} O ₂					74.1% after	
					2000 cycles	
					at 1 C	

6.2.5 Electrochemical Performance of Li/MP-NCM in Full Lithium Cell Configuration

To enhance the safety of lithium batteries and evaluate the compatibility of MP-coated NCM also with other electrolyte systems, we replaced in a next step the standard organic carbonate-based electrolyte with an ionic liquid-based one, precisely 0.2LiTFSI-0.8PYR₁₄FSI (Figure 6.6).

Figure 6.6a shows the cycling performance of MP-NCM-2wt% at 0.1C for 250 cycles after one formation cycle at 0.05C. The initial coulombic efficiency was as high as 94.0% at such low C rate, increasing subsequently to about 99% for the second and all following cycles with a specific discharge capacity of 152.3 mAh g⁻¹ for the first cycle at 0.1C. The capacity is slightly lower compared to those cells incorporating the standard electrolyte, which is assigned to the lower ionic conductivity of the ionic liquid-based electrolyte at 20 °C. Nonetheless, even after 250 cycles the cell provides a discharge capacity of 138.6 mAh g⁻¹, accounting for the remarkable capacity retention of 91.0%.

In Figure 6.6b, we present the results for MP-NCM-2wt%-based electrodes cycled at an elevated C rate of 0.5C for more than 2000 cycles, including a C rate test (0.05C to 3C) at the very beginning of the test and after about 1000 cycles. Once again, the cell provides lower specific capacities, particularly at elevated dis-/charge rates, compared to those cells employing the organic carbonate-based electrolyte because of the lower ionic conductivity at ambient temperature. In detail, the cell delivered specific capacities of 137.4,

119.2, 84.0, and 41.9 mAh g⁻¹ at 0.5, 1, 2, and 3C, respectively. Nevertheless, the capacity retention when getting back to 0.5C afterwards was as high as 99.0%, indicating a highly reversible lithium de-/intercalation behavior. This is further confirmed by the excellent capacity retention of 95.1% after 1000 cycles and still 85.4% after 2000 cycles, which is still well above the commonly mentioned “end-of-life” capacity of 80% of the initial value. It appears noteworthy to add that the rate capability was not significantly affected by such an extended cycling, revealing essentially similar capacity values as at the very beginning (Figure 6.6b).

This certainly outstanding cycling stability was further evidenced by subjecting MP-coated NCM to extended cycling at 1C (Figure 6.6c), revealing an initial capacity of 117.8 mAh g⁻¹ and excellent capacity retention of 98.7% after 1000 cycles and still 86.7% after 2000 cycles, while the coulombic efficiency was as high as 99.92%, which is a remarkably high value considering the fact that these tests were conducted with a lithium metal anode.

Figure 6.6 Galvanostatic cycling of MP-NCM, employing 0.2LiTFSI-0.8PYR₁₄FSI as alternative electrolyte: (a) Constant current cycling at 0.1C for 250 cycles after an initial formation cycle at 0.05C; (b) Constant current cycling at 0.5C for more than 2000 cycles after an initial C rate test, varying the dis-/charge rate from 0.05C to 3C, and including a second C rate test after 1000 cycles; (c) Constant current cycling at 1C for more than 2000 cycles after four formation cycles at 0.05C and 0.1C and including a second series of four cycles at 0.05C and 0.1C after 1000 cycles. The capacity retention after a selected number of cycles is provided in the corresponding panels.

6.3 Conclusions

In this work, we first successfully made a combination of SLP 30 graphite and MnPO₄@NCM₄₂₄ (MP-NCM) in full lithium-ion cell configuration. The as-prepared full lithium-ion cells exhibit excellent electrochemical performance

both in rate and long-term cycling performance. In detail, it reached a capacity of 142.0 (1 C), 132.0 (2 C), 114.4 (5 C) mAh g⁻¹. It is speculated that the superior high C-rate performance is ascribed to our choice of using MP-NCM with outstanding rate capability as the cathode material. A remarkable cycling stability for up to 2000 consecutive cycles was evidenced, together with a high energy density of 376 Wh kg⁻¹ and power density of 1841 W kg⁻¹. Even if considering of a 40 % penalty factor which is supposed to compensate for the weight of the electrolyte and all the ancillary components such as case, current collectors etc., our full lithium ion cells could still deliver a practical energy density of 226 Wh kg⁻¹. Such a value is substantially higher than that of the current Li-ion batteries.

Assembling lithium battery full-cells incorporating an ionic liquid-based electrolyte allows for outstanding cycling stabilities, achieving capacity retentions well above 85% even after 2,000 cycles.

Beside the potential realization of advanced high-energy and high-power lithium (-ion) batteries, we may anticipate that the herein reported strategy of applying a MnPO₄ coating can be readily employed also for other state-of-the-art and next generation cathode materials.

Chapter 7

Toward Greener Lithium-ion Batteries: Aqueous Binder-based NCM₄₂₄ Cathode Material with Superior Electrochemical Performance

This work reports a strategy towards greener lithium-ion batteries, by employing the aqueous sodium carboxymethyl cellulose-based NCM₄₂₄ (CMC/NCM) as cathode electrode. Compared with conventional organic PVDF-based electrodes, the CMC/NCM electrodes display very uniform distribution of NCM and carbon particles together with strong adhesion among the particles and with the current collector, leading to significantly mitigated crack formation and delamination of the electrode upon repeated delithiation/lithiation processes. As a result, CMC/NCM electrodes show good structural integrity. Additionally, these electrodes offer enhanced Li⁺ diffusion kinetics, reduced polarization, therefore, excellent high C-rate capability, and extremely stable cycling performance even at elevated temperature (60 °C). Moreover, benefiting from the features of low cost, environmentally friendliness, and easy disposability-recyclability, the water-soluble CMC is expected to be a promising binder for practical applicant in energy storage systems.

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7.1. Introduction

Currently, a global goal in battery technology is the exploration of greener and safer batteries with lower cost [273-275]. In the past decades, intensive efforts have been devoted to developing of LIBs, which have dominated the current consumable portable electronics and telecommunications market [244, 276-278]. Most of the studies focused on searching for alternatives of new active materials, new separators, new additives, modification of electrolytes, however, the investigation of binders for cathodes is apparently less investigated [279]. Even though the binder is electrochemically inert, it plays an important role in the electrode formulation and has a great impact on the electrode processing and performance.

In commercial LIBs, poly vinylidene difluoride (PVDF) is the conventional binder for the cathode materials (but it is much less used for the anode materials), owing to its good electrochemical stability as well as the good adhesion ability to bond the electrode materials and current collectors. However, PVDF has some serious drawbacks: 1) It is quite expensive, around 15-18 EUR kg⁻¹, considering industrial multiton scale [263, 272]; 2) It makes use of the volatile, toxic and expensive organic N-methyl pyrrolidone (NMP), resulting in safety concerns during the manufacturing process [52]; 3) Its disposal at the end of battery life is not easy; 4) It has a tendency to swell, gelify or dissolve into the organic carbonate based electrolyte, sometimes even forming gel-like polymer electrolyte with high viscosity, leading to desquamation of electrode particles and thus poor electrochemical performance [279, 280]. Therefore, new binders, which are environmentally friendly, cheap, easy for electrode processing and disposal, are searched.

Recently, the sodium salt of CarboxyMethylCellulose (CMC) has emerged as a promising alternative binder. CMC is generally produced by the insertion of carboxymethyl groups into natural cellulose. The water-soluble property of CMC undoubtedly is the biggest advantage over PVDF in which it allows the use of water as the solvent instead of the expensive and toxic NMP. Regarding

the industrial cost, that of CMC (1-2 EUR kg⁻¹) is only about tenth of PVDF, making CMC even more attractive [282]. In addition, the disposability of CMC based electrode at the end of battery life is much easier, compared to PVDF-based electrodes. The active material could be easily recovered by pyrolysis or, even better, dissolution (in water) of CMC binder, after the electrode material is removed from the current collector. Given these advantages, CMC has been wildly investigated as a replacement of conventional PVDF binder for lithium-ion batteries. However, more attentions of employing CMC as a binder have been focused on anode materials, such as graphite [283, 284], Si [285], LiTi₄O₁₂ [286], SnO₂ [287], Fe₂O₃ [288], NiO [289], MoS₂ [290] etc. To date, only few studies have reported CMC based cathode materials for lithium-ion batteries. Guyomard's group firstly employed CMC as aqueous binder for LiFePO₄, with homogeneous electrode morphology and identical performance with respect to the standard PVDF-based LFP [291]. Lux *et al.* studied LiFePO₄-based electrode with CMC serving as the binder, providing a possibility of developing greener and cost-effective LIBs [272]. Both high C-rate capability and long-term cycling stability of CMC-based electrodes were superior to those of PVDF-based electrodes. On the basis of this result, Kim *et al.* proposed full cell configuration of Li₄Ti₅O₁₂/LiFePO₄ (both were CMC-based) using ionic liquid PYR₁₄FSI as electrolyte with very stable electrochemical performance, even at elevated temperature (40 °C, 60 °C) [284]. CMC was also applied as a binder for high voltage LiNi_{0.4}Mn_{1.6}O₄ (5 V) cathodes, as reported in Wang's work [292]. The delivered capacity of CMC-based electrode was considerably higher than that of PVDF-based electrode due to more efficient electronic conductivity as well as more homogenous distribution of active material, conductive agent and binder. However, the PVDF system showed better cycling stability with 95% (vs. 89% of CMC-based system) of capacity retention after 100 cycles (1 C). In a more recent work, De Giorgio *et al.* [293], however, demonstrated as full graphite/LNMO cells in which both electrodes were CMC-based outperformed those based on PVDF, especially at elevated temperature. The

improved performance was found to be associated with the much thinner SEI forming on the CMC-based cathode by XPS and SEI measurements. Besides the olivine and spinel types of cathodes, CMC is also employed in layer cathodes. For example, Xu *et al.* compared the effect of CMC, PVDF and alginate-based NCM₃₃₃ cathode material on electrochemical performance [294]. The CMC-based NCM electrodes displayed the highest rate capability and cycling performance, even though the capacity at low current density was lower than that of PVDF and alginate based NCM. The superior cell performance was mostly ascribed to the lower activation energy of CMC-based electrode, which could facilitate the lithium-ions diffusion kinetics, yielding higher ionic conductivity.

To the best of our knowledge, there has been no report of the use of CMC as binder for NCM₄₂₄. Therefore, herein, we report the CMC-based bar-like NCM₄₂₄ electrode, which exhibits greener and cheaper characteristics, and lower processing cost and easier disposability-recyclability, together with good high C-rate capability, remarkable cycling stability and thermal stability.

7.2 Results and Discussion

Figure 7.1 compares the electrochemical performance of CMC-based and PVDF-based NCM electrodes. Undoubtedly, CMC-based NCM₄₂₄ (marked as CMC/NCM hereafter) showed considerably superior electrochemical performance over PVDF-based NCM₄₂₄ (denoted as PVDF/NCM hereafter). The rate capability test was performed via galvanostatic cycling at various C-rates, ranging from 0.1 C to 10 C, with five consecutive cycles for each step. As it can be seen from Figure 7.1a, PVDF/NCM delivered an initial discharge capacity of 166.2 mAh g⁻¹, *i.e.*, slightly higher than that of CMC/NCM (161.1 mAh g⁻¹). This may be attributed to the moderate leaching of Li and the transition metals (Ni, Co and Mn) occurring in aqueous slurries [295]. However, although PVDF/NCM displayed higher capacity at low to medium rates (from 0.1 C to 2 C), the capacity delivered at 10 C of CMC/NCM

exceeded PVDF/NCM (78.4 vs. 70.5 mAh g⁻¹). Interestingly, after high C-rate test, the capacity of the CMC/NCM electrode recovered to 133.8 mAh g⁻¹ at 1 C, *i.e.*, a capacity retention approaching 100.6%. In contrast, only a 97.6% capacity retention was achieved by the PVDF/NCM electrode. In order to examine the capacity retention ability, both CMC/NCM and PVDF/NCM electrodes were subsequently subjected to 100 cycles at 1 C after rate-capability test. Through the comparison, CMC/NCM displayed considerably more stable cycling performance with only 1% capacity fading, which is much lower than that of PVDF/NCM (19.4% of capacity fade).

Figure 7.1 Comparison of the electrochemical performance of CMC/NCM and PVDF/NCM electrodes. (a) Rate capability test; (b) and (c) cycling performance; (d) and (e) cycling performance at elevated temperature (60 °C).

To further compare the cycling performance, several cells of both CMC/NCM and PVDF/NCM samples were assembled and cycled at 0.1 C, 2 C and 10 C for 100 cycles (at each rate). It is noticeable that CMC/NCM showed extremely stable cycling performance (Figure 7.1b) with capacity retentions as high as 96.4% (0.1 C), 102.9% (2 C) and 111.8% (10 C). At higher current densities, *ca.*, 2 C, 10 C, the capacity retention ratios exceeded 100% after 100 cycles, which is the result of slower electrode wetting process due to the high compactness of CMC-based electrodes. On the contrary, PVDF/NCM only maintained 89.7%, 78.2% and 79.4% of initial capacities at 0.1 C, 2 C and 10 C (Figure 7.1c), respectively. For the investigation of the cycling stability at elevated temperature (60 °C), both systems were tested at 10 C for 100 cycles. Figures 7.1d and 7.1e display the selected charge/discharge profiles of CMC/NCM and PVDF/NCM, respectively. It is understandable that the thermal stability decreases with increased temperature due to the high activity of transition metal elements with electrolyte, which will cause more side reactions and lead to stronger capacity fading [294]. Therefore, as expected, there was a capacity decay in CMC/NCM. However, still 96.7% of initial capacity was delivered after 100 cycles. In addition, the charge/discharge voltage profiles of CMC/NCM upon the 100 cycles almost overlapped (Figure 7.1d), suggesting excellent reversibility. On the other hand, severe capacity and voltage decay were observed for PVDF/NCM (Figure 7.1e), indicating growing polarization upon cycling. Interestingly, the cycling performance of PVDF/NCM was abnormally more stable at 60 °C than 20 °C. This may be ascribed to accelerated Li^+ transport kinetics with increased operation temperature, leading to improved electrochemical performance.

The cycling stability at higher mass loadings ($\sim 4 \text{ mg cm}^{-2}$) were also compared as shown in Figure 7.2. Being subjected to 200 consecutive cycles at 2 C, still, CMC/NCM was able to retain 91.6% of initial capacity (Figure 7.2a). At higher mass loadings, the initial three cycles showed a slightly capacity decay of around 3 mAh g^{-1} . Afterwards, due to the slower electrode wetting, a

slightly capacity increase was evidenced and stabilized at around 104.7 mAh g^{-1} . For comparison, PVDF/NCM electrode with mass loading of ($\sim 4 \text{ mg cm}^{-2}$) was test under the same condition. Albeit a higher capacity was achieved, the capacity fading upon cycling was very severe (Figure 7.2b). Therefore, after 200 cycles, a substantially lower capacity retention ratio was obtained, *ca.*, 70.0%, delivering an even lower capacity of 90.6 mAh g^{-1} (*vs.* 98.2 mAh g^{-1} of CMC/NCM).

Figure 7.2 Cycling performance of (a) CMC/NCM, and (b) PVDF/NCM with higher mass loadings.

In order to understand the effects of the binder on electrochemical performance, cyclic voltammetry tests were performed to examine the electrochemical behaviour of CMC/NCM and PVDF/NCM systems. When swept at 0.1 mV s^{-1} in the voltage range of 2.5–4.5 V, one pair of redox peaks occurred in both systems. The initial three CV cycles of CMC/NCM showed higher peak current densities, reproducibility and reversibility (Figure 7.3a) than those of PVDF/NCM (Figure 7.3d). As it can be seen from Table 7.1, the initial anodic/cathodic peaks of CMC/NCM were located at 3.817 V and 3.700 V, respectively, with a redox peak separation of 0.117 V. After three cycles, the redox peak separation reduced to 0.056 V, suggesting very small polarization in

the CMC/NCM electrode. With the PVDF/NCM electrode, however, a relatively larger redox peak separation, *ca.*, 0.155 V, was observed in the first delithiation/lithiation process. Even after three cycles, the peak separation was about 0.1 V, *i.e.*, almost twice that of CMC/NCM electrode, indicating that higher polarization existed in the PVDF/NCM electrode. For the investigation of apparent lithium ions diffusion kinetics, CV curves at various scanning rates (0.1-1.5 mV s⁻¹) were also conducted (Figures 7.3b and 7.3e). Both systems showed a linear relationship of peak current intensity versus square root of scanning rate. Based on the Randles-Sevcik equation [90], the apparent lithium ion diffusion coefficients of CMC/NCM were to be 4.50×10^{-8} cm² s⁻¹ and 9.52×10^{-9} cm² s⁻¹ for the delithiation and lithiation processes, respectively. These values are over two folds those of PVDF/NCM (1.85×10^{-8} cm² s⁻¹, 4.85×10^{-9} cm² s⁻¹). The faster lithium ion transfer kinetics clearly explain the better high C-rate capability of CMC/NCM, comparing to PVDF/NCM.

Figure 7.3 Comparison of the electrochemical behaviour of CMC/NCM and PVDF/NCM electrodes. (a) and (d) Initial three cyclic voltammetry (CV) curves (0.1 mV s⁻¹); (b) and (e) CV curves at various scanning rates (see legend); (c) and (f) plots of current peak intensity versus the square root of the scan rate.

Table 7.1 Detailed information from CV results.

	1 st cycle		3 rd cycle	
	anodic/ cathodic (V)	peak separation (V)	anodic/ cathodic (V)	peak separation (V)
CMC/NCM	3.817/3.700	0.117	3.756/3.699	0.057
PVDF/NCM	3.877/3.722	0.155	3.822/3.722	0.100

The voltage profiles of the two electrodes upon galvanostatic charge/discharge cycles at different current densities are shown in Figure 7.4. During the initial three activation cycles at 0.1 C, the voltage profiles of systems exhibited almost ideal symmetry. As it can be seen from the last ten galvanostatic cycles when tested at 2 C in Figure 7.4a, CMC/NCM still showed nice symmetric voltage profiles, suggesting very low polarization and high reversibility. When testing at 10 C (Figure 7.4b), an increased voltage gap between the charge and discharge profiles is observed due to limited electrode kinetics. This problem, however, is already serious at 2 C for the PVDF/NCM electrode (Figure 7.4c), resulting from the sluggish Li^+ kinetics, which is in consistent with the CV results. At 10 C, the severe asymmetry of the voltage profiles is well evidenced in Figure 7.4d, implying that a very severe polarization existed, especially during discharge. This results in much less Li^+ to be re-inserted into the NCM host during discharging process. As a consequence, severe capacity fading upon cycling occurred. Figures 7.4e-g compare the corresponding differential capacity plots (last five cycles) of CMC/NCM and PVDF/NCM. The CMC/NCM electrode well maintained its profiles even at 10 C. In contrast, the intensity of the PVDF/NCM cathodic peak decreased substantially upon increasing rates. Also, at 2 C and 10 C very distorted profiles are presented. As expected, the redox peak separation showed a tendency to increase at higher current densities. Table 7.2 lists the detailed information obtained from the differential capacity plots. The separation increased from 0.015 V (0.1 C) to 0.049 V (2 C), and to 0.167 V (10 C) for the CMC/NCM electrode. However, much larger separations were observed in PVDF/NCM system, *ca.*, 0.043 V (0.1 C), 0.158 V (2 C), 0.243 V (10 C). These values provide quantitative proofs of the much severe polarizations occurring with the PVDF/NCM electrode, which justifies its inferior high rate capability and long-term cycling stability with respect to the CMC/NCM electrode.

Figure 7.4 Comparison of the voltage profiles versus time of (a) and (b) CMC/NCM; (c) and (d) PVDF/NCM galvanostatically cycled at 0.1 C and then either 2 C or 10 C; (e-g) differential capacity plots of CMC/NCM (red) and PVDF NCM (black).

Table 7.2 Detailed information obtained from differential capacity plots.

	0.1 C	2 C	10 C
	anodic/cathodic (V)	anodic/cathodic (V)	anodic/cathodic (V)
CMC/NCM	3.771/3.756	3.795/3.747	3.881/3.713
PVDF/NCM	3.786/3.744	3.877/3.719	3.938/3.695

In order to better understand the binder effect on the electrode performance, the morphology of the electrodes was examined by scanning electron microscope (SEM). Both systems were calendared under the same conditions. Figures 7.5a and b display the morphology of a CMC/NCM electrode at different magnifications, showing as the NCM bars were homogeneously distributed among the active carbon particles and binders. The surface of the electrode is very flat, indicating even thickness of the electrode

layer. However, a particle agglomeration phenomenon is seen in case of PVDF/NCM electrode (Figures 7.5c and d). Plenty of NCM particles were connected with very few or even without any conductive agent, which would cause poor electronic conductivity and thus seriously affect the electrochemical performance, particularly at higher current densities. The difference in electrode morphology of CMC/NCM and PVDF/NCM could be due to the thermoplastic characteristics of the PVDF binder favouring for the NCM particles to align parallel to the surface, while the compression of the CMC/NCM electrode does not affect the original morphology, leaving a more uniform but open morphology.

Figure 7.5 SEM images (at different magnifications) comparing the morphology of (a) and (b) CMC/NCM and (c) and (d) PVDF/NCM pristine electrodes.

Figure 7.6 Peel test of (a) and (c) CMC/NCM; (b) and (d) PVDF/NCM electrodes.

The adhesion property of the binder plays an important role on the electrochemical performance. Therefore, peel tests were conducted to compare the adhesion of CMC/NCM and PVDF/NCM. As shown in Figure 7.6b, almost all of the PVDF/NCM coating in the right side of the electrode (*i.e.*, the part subjected to peel test) was peeled off, with only some spots of active material left. In contrast, the difference between the pristine and tested areas of the CMC/NCM electrode is not obvious (Figure 7.6a). The colour of the peeled side appears darker, implying that some material was removed making the surface rougher, however, to a much lesser extent than the PVDF/NCM electrode. SEM images were taken to give a more direct view for comparison. Panel 7.6c displays the front view of the CMC/NCM electrode, confirming as almost no difference is observed between the peeled and pristine halves of the CMC/NCM electrode. Only the very surface layer of the coated electrode is removed. On the other hand, the coating of the PVDF/NCM electrode (Figure 7.6d and insert) was almost completely removed after peeling, leaving only tiny and isolated islands. These results indicate the better adhesion property of the CMC binder, which is expected to greatly alleviate the electrode exfoliation over repeated charge/discharge cycles.

Figure 7.7 SEM images comparing the electrode morphology of cycled electrodes (after 100 cycles at 0.1 C). Front views of (a) and (b) CMC/NCM and (d) and (e) PVDF/NCM electrodes at different magnifications; cross-sectional views of (c) CMC/NCM and (f) PVDF/NCM electrodes.

To validate our assumption, we also performed SEM characterization of electrodes after 100 cycles at 0.1 C (Figure 7.7). The front views of the CMC/NCM electrode show intact surface and uniformly distributed NCM and super C45 particles (Figures 7.7a and b). This leads to uneven (de)lithiation due to non-uniform current distribution occurring in different electrode areas, resulting in uneven strain in the coating. As a result, a striking gap between the PVDF/NCM electrode layer and the aluminum current collector is seen in Figure 7.7f. This exfoliation of the active material from the current collector. According to the cross-sectional view, the electrode layer is tightly adherent to the aluminum current collector. For the PVDF/NCM electrode, however, obvious cracks are observed on the surface (Figure 7.7e), possibly due to the particles agglomeration and conductive additive distribution, leading to some certainly results in the increased polarization severely deteriorating the electrochemical performance, even at low current densities. Therefore, to a large extent, the high adhesion property of CMC binder as well as the highly

homogeneous distribution of all the electrode materials are the reasons for the excellent high rate and long-term cycling performance of CMC/NCM.

Figure 7.8 Comparative HRTEM images of (a) and (b) CMC/NCM and (d) and (e) PVDF/NCM electrodes. The corresponding FFT patterns are also shown in (c) and (f), respectively.

For the investigation of structural integrity of the CMC/NCM and PVDF/NCM electrodes after cycling, high-resolution transmission electron microscopy (HRTEM) was performed. From the low magnification TEM images (Figures 7.8a and d), the CMC/NCM particle exhibits a more smooth and clean surface while the PVDF/NCM particle displays a rough and porous surface. At higher magnification, the CMC/NCM particle presents a crystalline structure with clear lattice fringes (Figure 7.8b), further validated by the corresponding FFT pattern (Figure 7.8c) showing the hexagonal structure. However, the FFT pattern of PVDF/NCM is highly disordered and is more like polycrystalline structure (Figure 7.8f), which may be due to severe transition metal dissolution, as reported by Zhang *et. al* [296]. Thus, simply substituting the conventional binder, PVDF, with CMC results in the improved structural integrity of NCM upon cycling. These results are in line with a previously published study comparing the performance of LNMO electrodes made with CMC and PVDF binders, which showed that the former binder can actually protect the active material particles [293].

7.3 Conclusions

This work reports the use of CMC as aqueous binder for 1D bar-like NCM₄₂₄, which exhibited superior high C-rate capability, long-term cycling stability and thermal stability over the conventional electrodes based on PVDF. The excellent electrochemical performance of CMC/NCM is attributed to faster lithium ion diffusion kinetics (two times faster than that of PVDF/NCM) and lower electrode polarization increase during cycling. These improvements are bound to the high adhesive property of CMC binder, which greatly mitigated the formation of cracks and exfoliation of electrode materials from Al current collector, ensuring good electronic conductivity networks, as well as to the already reported protective effect of CMC on the active material particles upon cycling. Additionally, CMC has many prominent advantages over PVDF, such as low cost, environmentally friendliness and easy disposability-recyclability

due to its water-soluble characteristics. No flammable, costly and toxic solvents need to be used during the electrode-making as well as active material recycling at the end of the battery life. Therefore, the employment of CMC, as well as other water-soluble, natural polymers, as a binder for NCM highlights a promising direction for the development of greener lithium ion batteries with excellent electrochemical performance.

Chapter 8

Conclusion and Future Work

This chapter draws a conclusion of the whole thesis work. At the end of this chapter, some recommended future works that include extending the coating strategy to Ni-rich NCM cathode materials (i.e., NCM₆₂₂), in depth understanding of the mechanism behind the coating effect, scaling up of sample preparation, and making agglomerated secondary particle are also provided.

8.1 Conclusion

This thesis aims to investigate layered NCM as cathode material for lithium ion batteries. The main focus was placed on the synthesis of NCM cathode material with high C-rate capability and stable long-term cyclability. To achieve this goal, we prepared 1D bar-like NCM₄₂₄ via a co-precipitation method and a subsequent calcination step. Four batches samples were prepared at different calcination temperatures (750 °C, 800 °C, 850 °C, 900 °C) in order to obtain the optimized electrochemical performance. The N-NCM-800 turned out to be the optimal sample which achieved significantly enhanced lithium ion diffusivity, and thus superior high C-rate capability and stable cycling performance, attributing to the merits of: 1) preferentially exposed the {010} electrochemically active facets, which provide more open structure for unimpeded Li⁺ migration; 2) the greatly reduced diffusion pathway of lithium ions because of the bar shape.

To further enhance the cell performance, especially for the long-term cycling stability, we applied a surface coating strategy to suppress detrimental side reactions and thus to stabilize the electrode/electrolyte interface. The amorphous MnPO₄ coating layer acts as an ideal protective layer to physically isolate the contact between the NCM active material and the electrolyte. Additionally, the MnPO₄ coating enhances the lithium de-/intercalation kinetics, as revealed by the enhanced apparent lithium ion diffusion coefficient based on multi-scan rate CV test. 2wt% of coating amount turned out to be the optimal condition. As a result, MP-NCM-2wt% based electrodes reveal greatly enhanced C rate capability and superior cycling stability – even under exertive conditions like extended operational potential windows, elevated temperature, and higher active material mass loadings.

In order to demonstrate our potential for future commercialization, we assembled full lithium ion cells consisting of commercial SLP 30 graphite as anode material and our MnPO₄-coated NCM₄₂₄ as cathode material to demonstrate our potential toward commercialization. The graphite/MP-NCM

full lithium ion cells we fabricated not only yielded remarkable long-term cycling stability (capacity retention ratio up to 74.1% over 2000 cycles at 1 C) but also achieved a maximum gravimetric energy density estimated as 376.2 Wh kg⁻¹, which is the highest reported so far, to the best of our knowledge. When evaluated in an intrinsically safer ionic liquid electrolyte system, the as-prepared full lithium metal cells demonstrated outstanding cycling stabilities with a capacity retention of well above 85% after 2000 cycles (0.5 C, 1 C).

To keep in pace with the current global trend that pursues for greener and safer battery applications, we pushed a step forward by simply replacing the conventional organic PVDF-based binder with aqueous CMC-based binder, the latter features with low cost, environmental friendliness, and easy disposability-recyclability, water-soluble property. Compared with conventional organic PVDF-based electrodes, the CMC/NCM electrodes exhibited excellent high C-rate capability, and extremely stable cycling performance even at elevated temperature (60 °C) due to: 1) very uniform distribution of NCM and carbon particles together with strong adhesion among the particles and with the current collector; 2) significantly mitigated crack formation and delamination of the electrode upon repeated delithiation/lithiation processes; 3) enhanced Li⁺ diffusion kinetics, reduced polarization etc., making CMC a promising binder for practical application in greener and safer energy storage systems.

8.2 Recommended Future Work

8.2.1 Application of MnPO₄ Coating for Ni-rich NCM

8.2.1.1 Preliminary Result: MnPO₄-coated NCM₆₂₂ with Superior Long-term Cycling Stability at Elevated Temperature and High Voltage

As we mentioned in earlier chapters, to fulfill the rapidly growing demands for higher rate capability, higher energy density with longer cycling life for advanced LIBs so that EVs (HEVs or PHEs) are capable of running faster with longer travel distances, researchers try to increase the Ni content to

offer higher capacity and energy density. Among the nickel-rich $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$ series, NCM_{622} , which can deliver 170 mAh g^{-1} capacity in the range of 3.0 – 4.3 V, rendering it the most promising candidate for the next generation of advanced high-energy LIBs [84, 297]. Additionally, *Ab initio* calculations as well as experimental revealed that NCM_{622} has the highest Li-ion diffusion coefficient within the NCM series [254]. Nevertheless, structural degradation of NCM_{622} is quite apparent upon cycling, especially at high temperature and for higher cut-off voltages, due to the occurrence of detrimental side reactions at the electrode/electrolyte interface. The deterioration of NCM_{622} as cathode material will be accelerated, leading to continuous capacity decay and thus inferior electrochemical performances [41].

With our previous success in MnPO_4 -coated NCM_{424} , herein, we have plans to apply our coating strategy for Ni-rich NCM, such as NCM_{622} , NCM_{71515} , NCM_{811} etc., keeping pace with the current research trend particularly for industry field. By far, we have got some preliminary result about NCM_{622} , which will be discussed in detail in the following session.

Results and Discussion

Materials Characterization

Figure 8.1 displays XRD patterns of bare NCM (black line) and MP-NCM (red line) powders, respectively. Both diffractograms are in good agreement with the $\alpha\text{-NaFeO}_2$ layered structure ($R(-)3m$) without any impurities (JCPDS no. 74-0919 of LiNiO_2) [298]. The sharp reflections and well resolved splitting of the (006)/(102) and (108)/(110) reflections indicate a high degree of crystallinity and a well-ordered layered structure. Moreover, the identical XRD patterns obtained before and after applying the MnPO_4 coating confirms that this additional processing step does not have any impact on the bulk structure,

indicating that the coating layer remains on the particle surface. Furthermore, no additional reflections are observed for MP-NCM, suggesting that the coating is amorphous or quasi-amorphous, while the overall coating content is generally quite low.

Figure 8.1 XRD diffractograms of NCM (black line) and MP-NCM (red line), including the JCPDS reference card no. JCPDS 74-0919 for indexing the recorded reflections.

Scanning electron spectroscopy (SEM) and transmission electron microscopy (TEM) measurements were conducted to examine the morphology changes before and after applying the MnPO_4 coating (Figure 8.2). Non-coated NCM (Figures 8.2a-c) shows irregular submicron-sized particles with rather clean and smooth surface. After coating, there's no obvious change, except that the surface of MP-NCM becomes rougher, as can be seen from Figures 8.2d-f. This provides a first evidence for the successful synthesis of manganese phosphate coated NCM_{622} .

Figure 8.2 Typical SEM images of: (a) and (b) NCM, (d) and (e) MP-NCM; TEM images of (c) NCM and (f) MP-NCM.

In order to further support the formation of the MnPO_4 coating and to examine the influence of the coating layer on the base NCM material, XPS analysis was employed before and after the coating (Figure 8.3). First of all, the presence of all elements, *i.e.*, Li, Ni, Co, Mn and O, is corroborated in both the samples from the survey scan spectra shown in Figure 8.3a, where the P 2p peak is only detected in the spectrum of MP-NCM, due to the presence of the MnPO_4 coating. As mentioned, no peak belonging to P is seen for the former material (Figure 8.3b), while a characteristic peak is seen for the coated sample at 133.3 eV, which is the typical position of a metal phosphate peak. Figure 8.3c displays the Mn 2p detail spectra of both samples (before and after coating). The Mn 2p_{3/2} peak is located at 642.2 eV for the uncoated sample and

at 642.5 eV for the coated sample. A comparison with the mean values for MnO (641.2 eV), Mn₂O₃ (641.7 eV), and MnO₂ (642.3 eV) in the NIST XPS database points to a tetravalent oxidation state of the Mn in both samples. It should be noted that this comparison does not take into account possible shifts due to the change in the chemical environment of the mixed oxides, which might be also responsible for the slight upshift of the peak position in the coated sample. The Mn oxidation state was further investigated by the Mn 3s peak splitting (Figure 8.3d), since it has been shown that the degree of the peak splitting can be used to determine the Mn oxidation state: the separation is ~4.7 eV for Mn⁴⁺ in MnO₂, increases to ~5.3 eV for Mn³⁺, and reaches values around 6 eV for Mn²⁺ [299, 300]. In the present case, the splitting amounts to 4.5 and 4.6 eV for the NCM and MP-NCM samples, corroborating the earlier assessment of tetravalent Mn, while the slightly higher peak splitting in case of MP-NCM may indicate a slightly lower oxidation state – presumably as a result of the presence of the manganese phosphate coating. The Ni2p_{3/2} peak (Figure 8.3e) shows binding energies of 854.4 eV for NCM and 854.5 eV for MP-NCM, indicating a bivalent state of Ni in both cases. The Co 2p_{3/2} peak (Figure 8.3f) appears at 779.8 eV (NCM) and 779.9 eV (MP-NCM), respectively, a typical value for oxidized Co. Furthermore, the absence of prominent satellite peaks at ~786 and ~802 eV, which are characteristic features for Co²⁺ but do not exist for Co³⁺, demonstrates that Co is trivalent in both samples.

Figure 8.3 XPS spectra of NCM (black line) and MP-NCM (red line). (a) Survey scan, (b) P 2p region, (c) Mn 2p region, (d) Mn 3s region, (e) Ni 2p region, and (f) Co 2p region.

Cyclic Voltammetry and Apparent Lithium-Ion Diffusion

Figures 8.4a and d display the first and third cyclic voltammogram curves of NCM and MP-NCM, respectively, at a scan rate of 0.1 mV s^{-1} . The main redox peaks, which appear in the range of 3.7 – 4.0 V correspond to the $\text{Ni}^{2+}/\text{Ni}^{4+}$ redox couple. Figure 8.4d reveals an Additional pair of weak cathodic/anodic peaks located around 2.7 – 3.0 V, which is assigned to the $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox couple in manganese phosphate, providing also electrochemical evidence that the surface is coated by MnPO_4 . A detailed

information of the $\text{Ni}^{2+}/\text{Ni}^{4+}$ redox couple are listed in Table 8.1. As listed therein, the initial anodic peak and cathodic peak are located at 3.897 V and 3.715 V with an interval peak separation of 0.182 V. For MP-NCM, the peak separation is slightly higher (0.188 V) initially, but decreases to 0.163 V after three cyclic sweeps. In contrary, for NCM the peak separation increases upon cycling, *i.e.*, to 0.209 V after three cyclic sweeps. Such a decreased polarization for the coated material is expected to have a positive effect on the electrochemical performance. In fact, the peak intensity for MP-NCM showed an increase during the initial three cycles, indicating a material activation. On the contrary, NCM showed an obvious current intensity drop, implying that the irreversible capacity is more severe before coating. It may be speculated that the coating layer can somehow facilitate the formation of a more uniform and thinner cathode electrolyte interphase (CEI). In order to examine the coating effect on the lithium ion transfer kinetics, the CV scans at various scan rates from 0.1 to 1.5 mV s^{-1} were performed to calculate the apparent lithium ion diffusion coefficient (Figures 8.4b and e). For both, NCM and MP-NCM, the CV profiles at higher scan rates are well maintained, showing a linear relationship of the peak current intensity versus the square root of the scan rate (Figures 8.4c and f). The apparent lithium ion diffusion coefficients were calculated according to the Randles-Sevcik equation [101]. The calculated results, listed in Table 8.1, show significantly enhanced apparent lithium ion diffusivities, *i.e.*, 2.17×10^{-8} and $5.66 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ for delithiation and lithiation processes, almost four times fastened compared with NCM (*ca.*, 5.24×10^{-9} and $1.87 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, respectively). Obviously, the amorphous coating layer of MnPO_4 allows for a fast Li^+ delivery to/from the NCM surface. Therefore, it is reasonable to expect that MP-NCM electrodes can yield an improved high C-rate capability and long-term cycling stability.

Figure 8.4 Results of cyclic voltammetry measurements for NCM and MP-NCM: (a) and (d) the first three cycles for NCM and MP-NCM, respectively, at a scan rate of 0.1 mV s⁻¹; (b) and (e) CV curves at various scan rates; (c) and (f) the corresponding linear plot of the peak current density as a function of the square root of the corresponding scan rate.

Table 8.1 Comparative detailed information of NCM and MP-NCM from CV results.

	1 st cycle		3 rd cycle		apparent lithium ion diffusion coefficient	
	Anodic/Cathodic (V)	Peak Separation (V)	Anodic/Cathodic (V)	Peak Separation (V)	Delithiation (cm ² s ⁻¹)	Lithiation (cm ² s ⁻¹)
NCM	3.897/3.715	0.182	3.905/3.696	0.209	5.24x10 ⁻⁹	1.87x10 ⁻⁹
MP-NCM	3.888/3.700	0.188	3.873/3.709	0.163	2.17x10 ⁻⁸	5.66x10 ⁻⁹

Galvanostatic Cycling and Rate Capability

To investigate the impact of the coating on the cycling performance in more detail, electrodes of NCM and MP-NCM were tested at various C rates (0.1C, 2C, and 10C) over 100 cycles each. Figure 8.5 depicts selected charge/discharge profiles for these electrodes based on NCM or MP-NCM. The profiles in Figures 8.5a and d reveal that the initial discharge capacities of NCM and MP-NCM lower current density (0.1 C) are 182.6 and 179.4 mAh g⁻¹, respectively, leading to initial Coulombic efficiencies of 93.3% and 94.0%. The slightly lower capacity of MP-NCM is largely attributed to the presence of the coating layer, since its mass is included for the calculation of the specific capacity. Nonetheless, a capacity retention of 93.1% was achieved after 100 cycles, which is much higher than that achieved for NCM (89.1%). The difference of cycling stability between NCM and MP-NCM becomes more obvious at higher current densities. For instance, after 100 cycles, MP-NCM still provides 143.4 mAh g⁻¹ at 2C (Figure 8.5e) and 126.2 mAh g⁻¹ at 10C (Figure 8.5f) with only 5.3% and 2.3% capacity decay after 100 cycles. On the contrary, the uncoated material delivered only 135.0 (2 C, Figure 8.5b) and 117.5 mAh g⁻¹ (10 C, Figure 8.5c), with capacity retention ratios of 85.5% and 87.5%, despite the slightly higher initial capacity. Furthermore, the electrode polarization is greatly reduced after coating upon cycling, particularly at higher C-rates, *ca.*, 2 C and 10 C (Figures 8.5b, c, e and f). This greatly enhanced cycling stability is further highlighted by studying electrodes with an increased mass loading of 12 mg cm⁻², for which a capacity retention of 90.7% is maintained after 100 cycles at 1C (Figure 8.6).

Figure 8.5 Selected dis-/charge profiles for electrodes based on NCM and MP-NCM at various C-rates – all cells were subjected to 100 dis-/charge cycles: (a) and (d) 0.1C; (b) and (e) 2C; (c) and (f) 10C.

Galvanostatic Cycling at Elevated Temperature

In order to evaluate the thermal stability, both the NCM and MP-NCM electrodes were cycled at 10 C for 100 cycles at 40 °C (Figure 8.7b) and 60 °C (Figure 8.7c), respectively. At 40 °C, MP-NCM electrode revealed a specific capacity of 155.4 mAh g⁻¹ with 94.0% capacity retention ratio after 100 cycles at 10 C, while NCM electrode delivered a lower capacity (151.1 mAh g⁻¹) with only 87.6% capacity recovery ratio. Compared to room temperature performance, the increased capacity delivered at elevated temperature can be explained by an accelerated Li⁺ de-/intercalation ability. When further

increasing the temperature up to 60 °C, the MP-NCM electrode yielded a greatly enhanced capacity retention ratio (83.1%) compared with bare NCM (68.8%) after 100 cycles, indicating that the thermal stability of MP-NCM is significantly enhanced after coating. This is attributed to a considerably better suppression of the occurring side reactions at the electrode/electrolyte interface due to the manganese phosphate coating layer and the strong covalent P-O bonding in PO₄. The significantly enhanced thermal stability allows the MP-NCM electrodes to work in a wider range of operation temperature with outstanding electrochemical performance.

Figure 8.6 Galvanostatic cycling of MP-NCM-based electrodes with an increased mass loading of 12 mg cm⁻²; the first three cycles were conducted a 0.1C (cut-off voltages: 3.0 and 4.3 V).

Galvanostatic Cycling with an Increased Anodic Cut-Off Voltage

To evaluate the cycling stability for extended voltage ranges, both NCM and MP-NCM electrodes were tested at various C rates (0.1C to 10C) and subjected to 50 cycles at 0.1C and 10C, respectively, while increasing the anodic cut-off voltage to 4.6 V. Figure 8.8a compares the rate capability of NCM and MP-NCM. Initially, the capacity of MP-NCM at 0.1 C (221.0 mAh g⁻¹) slightly exceeded NCM (215.8 mAh g⁻¹). With the increasing current densities, the discharge capacities of MP-NCM electrode were 196.2, 182.0,

151.5, 136.4 and 114.5 mAh g⁻¹ at 0.5 C, 1 C, 2 C, 5 C and 10 C, respectively. On the contrary, strong capacity degradation is observed for NCM, *i.e.* 175.1 (0.5 C), 151.6 (1 C), 124.2 (2 C), 80.0 (5 C), 22.9 (10 C) mAh g⁻¹. When returning to 1C after this C rate test, MP-NCM still retained 94.5% capacity, while NCM only recovered to 73.2%. Generally, the limiting factor of rate capacity is the delivery of Li-ions and electrons to the surface as well as the bulk diffusion of the lithium ions [301, 302]. Consequently, the electrochemical polarization gets worse under high rate situation. The cycling performance is less stable within the voltage range of 3.0 – 4.6 V. Nevertheless, MP-NCM still recovered 86.9% and 70.7% of initial capacity at 0.1 C and 10 C after 50 cycles, respectively. As for NCM, only 67.4% of initial capacity was retained at 0.1 C and essentially no capacity was delivered after around 35 cycles at 10 C (Figure 8.8b).

Table 8.2 listed the reported electrochemical performance of NCM₆₂₂ with various coating materials within the past three years. Given the voltage range (3.0 – 4.3 V), our MP-NCM showed a comparatively high capacity, compared to those reported previously. By comparison, the room temperature cycling stability at low current densities of our MP-NCM outperforms the majority of those reported materials. It is especially notable that MP-NCM shows such an excellent high C-rate cycling performance (at 10 C), which has never been reported so far, even under circumstances of elevated temperature (60 °C) and high cut off voltage (4.6 V). The significantly improved rate capability of the MP-NCM electrode is mainly ascribed to the amorphous coating layer of MnPO₄ with appropriate coating amount, which facilitates Li⁺ transport across the surface. This result is in consistence with our CV result as discussed in previous section. The structural instability is quite normal phenomena at high operation voltages. However, it is greatly suppressed after coating, presumably due to the greatly reduced transition metal's dissolution, contributing to the significantly enhanced electrochemical performance.

Figure 8.7 Comparative thermal stability upon 100 cycles at 10 C between NCM and MP-NCM at different temperatures: (a) 20 °C; (b) 40 °C and 60 °C.

Figure 8.8 Comparative electrochemical performance between NCM and MP-NCM (a) rate capability and (b) cycling stability at 0.1 C and 10 C for 100 cycles in the voltage range of 3.0 – 4.6 V.

Investigation of the Structural Stability with Increasing Temperatures by In Situ HT-XRD Analysis

Figure 8.9 compares the evolution of the XRD diffractograms for charged (4.3 V) electrodes based on NCM (Figure 8.9a) and MP-NCM (Figure 8.9b) when heated from 30 to 600 °C. Due to the rather small electrode size, not fully covering the sample stage, and the presence of the graphite dome, covering the electrode, all final diffractograms contain some contributions from the heating stage and the graphite dome (Figure 8.10). In case of the NCM electrode (Figure 8.9a), no structural changes were observed below 200 °C. Within this temperature range, the (003)_L and (104)_L intensities and the ratio of (003)_L/(104)_L remained unchanged, suggesting that Ni ions are not displaced to the Li slabs [303]. Above 250 °C, the disappearance of the (003)_L reflection and

the merging of the $(108/110)_L$ reflections indicates the onset of the phase transition from a layered structure ($R(-)3m$) to a disordered spinel structure (LiMn_2O_4 -type, $Fd(-)3m$) [303]. However, the occurrence of the $(220)_{RS}$ reflection as well as the shoulder at the right hand side, which belongs to metallic nickel at 400 °C, indicate a further progress of the phase transition to a rock-salt type structure ($Fm(-)3m$) [304]. With the MnPO_4 coating layer, for the MP-NCM electrode (Figure 8.9b), we observed a substantially delayed phase transition from the layered structure to the spinel structure and the onset temperature increased to above 300 °C, as reflected by the appearance of the $(111)_{S1}$ reflection of the disordered LiMn_2O_4 -type spinel structure and the subsequent appearance of the $(111)_{S2}$ peak of the Mn_3O_4 -type spinel structure at around 600 °C [39]. Unlike the bare NCM electrode, no further phase transition to the rock-salt phase is observed for the MP-NCM electrode. The contour plots of selected reflections, *e.g.*, $(003)_L$ and $(104)_L$ as shown in Figure 8.11, provide more direct visual evidence of the significantly delayed phase transitions of the MP-NCM electrode, highlighting the substantially enhanced thermal stability after coating the NCM_{622} particles with MnPO_4 .

Figure 8.9 *In situ* HT-XRD diffractograms recorded for electrodes based on (a) NCM and (b) MP-NCM in their charged state (4.3 V).

Figure 8.10 XRD diffractograms of (a) the heating stage together with graphite dome and (b) the heating stage only.

Figure 8.11 Contour plots the evolution of the (003) and (104) reflections upon heating from 30 to 600 °C for charged (4.3 V) electrodes based on (a) NCM and (b) MP-NCM.

Investigation of the Structural Stability with Increasing Temperatures by Differential Scanning Calorimetry Analysis

Differential Scanning Calorimetry (DSC) measurements were also conducted to examine the changes of the thermal behavior before and after applying the manganese phosphate coating. Also for these experiments, we used NCM and MP-NCM electrodes charged to 4.3 V. The thermal stability is a highly important issue for nickel-rich NCM, particularly in the fully charged state. Figure 8.12 compares the DSC curves of NCM and MP-NCM. Upon heating, the instability of Ni^{4+} (Co^{4+}) at highly delithiation state becomes more serious [192]. Therefore, oxygen is liberated from the transition metal oxide layers, triggering the electrolyte oxidation [304]. The DSC profile of NCM shows a main exothermal peak centered at 282.0 °C, together with a smaller peak centered at 274.0 °C, generating 307.4 J g⁻¹ heat. After coating, the onset decomposition temperature of MP-NCM shifts to higher temperature, *ca.*, 285.6 °C, with a lower heat evolution (264.6 J g⁻¹). This result indicates that our amorphous coating layer is capable of preventing direct contact between the electrolyte and the highly unstable oxidized positive electrode, and thus decreasing the severity of an exothermic reaction, *i.e.*, suppressing unwanted surface reactions. This significantly enhanced thermal stability, introduced by the MnPO_4 coating layer, is the supposed to be the main reason for the outstanding electrochemical performance of the coated electrode MP-NCM at elevated operation temperatures.

Figure 8.12 DSC profiles of charged electrodes (4.3 V) based on NCM (in black) and MP-NCM (in red) as active material.

Table 8.2 Performance comparison with other reported NCM₆₂₂ with different coating materials.

Coating material	Voltage (V)	Capacity (mAh g ⁻¹)	Capacity retention (RT)	Capacity retention (high T)
MnPO ₄ (THIS WORK)	3.0–4.3	179.4 (0.1 C)	93.1% (0.1C) after 100 cycles; 94.7% (2C) after 100 cycles; 97.7% (10C) after 100 cycles;	94.0% (10C, 40 °C) after 100 cycles; 83.1% (10C, 60 °C) after 100 cycles;
	3.0–4.6	221.0 (0.1 C)	86.9% (0.1C) after 50 cycles; 70.7% (10C) after 50 cycles;	---
Ethoxy-functional polysiloxane [40]	2.8–4.3	176.2 (0.2 C)	93.1% (1C) after 200 cycles;	84.9% (1C, 55 °C) after 100 cycles;
Co ₃ O ₄ [41]	2.8–4.6	209.5 (0.1 C)	60.3% (1C) after 100 cycles;	---
NaTi ₂ (PO ₄) ₃ [199]	3.0–4.5	187.9 (0.2 C)	85.0% (charge 1C/discharge 2C) after 150 cycles;	---
	3.0–4.6	206.3 (0.2 C)	85.3% (charge 1C/discharge 2C) after 100 cycles;	---
MOF-derived alumina [37]	3.0–4.5	214.6 (0.2 C)	92.7% (1C) after 100 cycles;	---
Mn ₃ PO ₄ [124]	3.0–4.3	173 (0.1 C)	93.3% (0.5C) after 50 cycles;	90.9% (0.5C, 60 °C) after 50 cycles;
	2.8–4.3	184.1 (0.1 C)	90.4% (1C) after 150 cycles;	85.1% (0.5C, 60 °C) after 150 cycles;
Al ₂ O ₃ [305]	2.8–4.4	172.2 (1 C)	87.9% (1C) after 150 cycles;	---
	2.8–4.5	177.6 (1 C)	81.1% (1C) after 150 cycles;	---
TiO ₂ [306]	2.5–4.3	187.7 (0.1 C)	85.9% (1C) after 100 cycles;	80.8% (1C, 55 °C) after 100 cycles;
Al ₂ O ₃ &PEDOT-co-PEG [36]	2.6–4.3	167.0 (0.5 C)	96.0% (0.5C) after 100 cycles;	94.3% (0.5C, 55 °C) after 100 cycles;
SiO ₂ [125]	3.0–4.3	175 (0.1 C)	97% (0.5C) after 50 cycles;	93% (0.5C, 60 °C) after 50 cycles;
PEDOT-co-PEG [31]	2.8–4.3	184.3 (0.1 C)	93.9% (0.5C) after 100 cycles;	91.0% (0.5C, 55 °C) after 100 cycles;
TiO ₂ [307]	2.5–4.3	195.5 (0.2 C)	87.7% (1C) after 50 cycles;	---
Al ₂ O ₃ [308]	3.0–4.3	197.1 (1 C)	95.0% (1C) after 30 cycles;	---
	3.0–4.5	184.8 (1 C)	91.0% (1C) after 30 cycles;	---

Ex situ TEM Analysis

TEM images of MP-NCM electrode after 100 cycles at 0.1 C is given in Figure 8.13. From the low magnification TEM image, we can see that the MP-NCM particles exhibit almost intact morphology with relatively smooth surface demonstrated in Figure 8.13a, indicating that structural integrity is well maintained after cycling. At higher magnification (Figure 8.13b), a clear uniform and thin layer of CEI (2-3 nm) is formed on the surface of MP-NCM through the decomposition of electrolyte. Between the CEI layer and the surface of NCM, a relatively homogeneously distributed MnPO_4 layer still exists, even after 100 continues cycles. The presence of MnPO_4 prohibits the side reactions, HF attack, and lead to greatly reduced transition metals' dissolution, ensuring good structural integrity. Consequently, it will lead to significantly improved electrochemical performance.

Figure 8.13 (a) and (b) TEM images of MP-NCM electrode after 100 cycles at 0.1 C.

Conclusions

In conclusion, we designed and successfully synthesized MnPO_4 -coated NCM_{622} (MP-NCM) with a significantly improved electrochemical performance. The MP-NCM electrodes achieved an excellent cycling stability with 93.1%, 94.7%, and 97.7% capacity retention after 100 cycles at 0.1C, 2C,

and 10C, respectively. Even at higher testing temperatures, MP-NCM showed a remarkable stability over 100 cycles, with 94.0% (40 °C) and 83.1% (60 °C) capacity retention. These latter values are much higher than those for NCM, which retained only 87.6% at 40 °C and 68.8% at 60 °C. Also when tested with elevated anodic cut-off voltages (3.0 – 4.6 V), the MnPO₄ coating substantially improves the rate capability and cycling stability. The capacity retention upon cycling increases from 67.3% to 86.9% after 50 cycles at 0.1C. Even at 10C, MP-NCM still maintained 70.7% of the initial capacity, while no capacity was delivered for NCM. According to the CV results, the MnPO₄ coating layer cannot only physically isolate the contact with the electrolyte and thus reduce the transition metal dissolution into the electrolyte, leading to an excellent long-term cycling stability of MP-NCM, but moreover improves the ionic transport kinetics. In addition, the strongly covalent nature of the PO₄ bonding has a beneficial influence on the thermal stability as confirmed by both DSC and *in situ* HT-XRD measurements, granting an excellent cycling stability also at elevated operation temperatures and anodic cut-off voltages. Overall, the superior electrochemical performance of MP-NCM makes it a highly potential candidate for practical lithium-ion battery applications – not least due to the very facile and versatile synthesis route.

8.2.2 In Depth Investigation of Mechanism Behind the Surface Coating

Although we have conducted some *in situ* and *ex situ* analysis trying to understand why the cell performance is significantly enhanced after coating. However, more thorough and fundamental investigations are still needed in order to figure out the authentic mechanism. In the future, some *in situ* and *ex situ* technologies will be adopted. For instance, by combining *in situ* and *ex situ* XRD measurements, the possible phase transitions (*i.e.*, from layered to spinel and to rock-salt structure) upon galvanostatic cycling might be evidenced in case of none coated sample. The comparative result between coated and none-coated sample could give a strong guidance for the mechanism behind the cell

performance enhancement. *In situ* TEM could reveal changes in terms of both structure and morphology upon charging and discharging. Besides, the growth of solid interface electrolyte (SEI) layer could be possibly detected. The combination of *ex situ* TEM and focused ion beam (FIB) technique would offer a direct view of possible crack generations.

8.2.3 Follow Up Investigation of Cycling Stability in Ionic Liquid Electrolyte System

In Chapter 6, we have demonstrated the extremely stable cycling performance of Li/MP-NCM₄₂₄ in full lithium cell configuration. The successful combination of the intrinsically greener and safer ionic liquid-based electrolyte, precisely 0.2LiTFSI-0.8PYR₁₄FSI, with NCM₄₂₄ have marked a step forward in green and safety batteries applications. Since my future works will mainly shift from NCM₄₂₄, over NCM₆₂₂ and eventually to NCMs with even higher nickel contents (*i.e.*, NCM₇₁₅₁₅, NCM₈₁₁, NCM₉₀₅₀₅ etc.). The high capacity of nickel-rich NCM will make up for the less capacity delivered in ionic liquid electrolyte system, with respect to the conventional organic electrolyte system. Therefore, the further follow up investigation about nickel-rich NCMs in ionic liquid electrolyte system would not only meet the demands for higher safety but also promote the request for higher energy densities.

Up to now, all the related measurements were conducted at 20 °C. However, in some particular cases, the requirement of batteries operation in some extreme temperatures spurs us to test cells under abuse conditions. Therefore, in future, it will also be very interesting to conduct some long-term cycling test under a wide range of temperatures, for instance, from -20 to +60 °C.

8.2.4 Scaling Up of Sample Preparation and Making Agglomerated Secondary Particle

Compared with other lab-scale material synthesis methods, our synthesis

route is very simple, cheap with rather high yield, *ca.*, 4 g powder per batch. However, to be employed in a real battery line, the very beginning challenge starts with scaling up of the material synthesis, *i.e.*, at kg scale. So, our future work will focus on the scalability of our cathode material synthesis. However, considering of kg scale sample preparation, it is highly possible to encounter the following questions or challenges: 1) How to synthesize NCM with homogenous particle size with narrow particle size distribution? This might involve with a careful control with stirring speed and reaction time to form homogenous precipitants. 2) How to synthesize NCM cathode material with stoichiometric components of each element, *ca.*, Li, Ni, Co, Mn and O? The stoichiometric components of Ni, Co and Mn should be controlled during co-precipitation step. Due to different precipitant rates of MCo_2O_4 ($\text{M}=\text{Ni, Co, Mn}$), generally, the Ni^{2+} is mostly difficult to fully precipitated. Therefore, the concentration of starting solution, the ratio of water: ethanol, and reaction time or even the input ratio of each starting materials ($\text{M}(\text{Ac})_2$, $\text{M}=\text{Ni, Co, Mn}$) need to be carefully adjusted. To achieve stoichiometric Li within NCM, the amount of LiAc starting material as well as the calcination process (temperature, time) need to be optimized to compensate for the lithium evaporation during calcination step. Generally, both air or oxygen atmosphere are fine for small scale sample preparation. However, when it comes to the kg scale sample preparation, oxygen atmosphere might become necessary to avoid the formation of oxygen-deficit product. A simultaneous stirring/mixing upon calcination step would be great helpful to yield uniform and homogenous NCM powders. 3) What's the optimized calcination condition? Shifting from g to kg scale might result in totally different calcination conditions, including heating rate, calcination time/temperature, atmosphere and so on.

Compared to commercial NCM samples, which are generally a mixture of big and small microspheres to obtain high tap density, our NCM sample has lower tap density due to the oriented property of the 1D bar-like morphology. For practical applications, a high tap density is quite important parameter in

order to get a high volumetric energy density. Therefore, to improve our sample's tap density, in future, we may try to employ a subsequent spray drying step after calcination to prepare secondary spherical particles, demonstrating our higher potential toward commercialization.

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First-Author Publications

1. **Z. Chen**, G.-T. Kim, Y. Guang, D. Bresser, T. Diemant, Y. Huang, M. Copley, R. J. Behm, S. Passerini, Z. Shen, “Manganese Phosphate coated $\text{Li}[\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}]\text{O}_2$ Cathode Material: Towards Superior Long-term Cycling Stability at Elevated Temperature and High Voltage”, **J. Power Sources**, 402 (2018) 263-271.
2. **Z. Chen**, G.-T. Kim, D. Bresser, T. Diemant, J. Asenbauer, S. Jeong, R. J. Behm, M. Copley, Z. Shen, S. Passerini, “ MnPO_4 -coated $\text{Li}(\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4})\text{O}_2$ for lithium (-ion) batteries with outstanding cycling stability and enhanced de-/lithiation kinetics”, **Adv. Energy Mater.**, 8 (2018) 1801573-1801585. (Selected as back cover)
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