# **Structure, Morphology and Reaction Mechanisms of Novel Electrode Materials for Lithium-ion Batteries**



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## **Statement of Length**

This dissertation does not exceed the regulation length of 60,000 words, including tables, references and appendix, but excluding pictures and diagrams.

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# **Structure, Morphology and Reaction Mechanisms of Novel Electrode Materials for Lithium-ion Batteries**

### Xiao Hua

## **Summary**

For the  $Li_{1+x}V_{1-x}O_2$  materials, the amount of excess Li does not change the average crystal structure; however, it alters the cycling performance greatly. This suggests that the local structure governs the electrochemical behaviour. This motivated us to employ the pair distribution function (PDF) technique to probe the local structure. The analyses show the displacements of  $V^{3+}$  form trimers. A structure model for the stoichiometric LiVO<sub>2</sub> incorporating the  $V^{3+}$  distortion was constructed and refined, to assist in the assignment of the Li sites revealed by the <sup>6</sup>Li nuclear magnetic resonance (NMR) results. For the TiO<sub>2</sub>-B materials, previous investigations of nanostructured phases suggested the Li insertion mechanism of these materials has a morphological dependence. However, the morphology of the nanoparticles, which to date shows the best cycling performance among all the TiO<sub>2</sub> phases with various morphologies, has not been well studied due to the technical challenges which arise from the nature of the diffraction technique and the limited particle sizes. We therefore employed techniques including small-angle X-ray scattering (SAXS) and PDF analyses, to provide an accurate description of the morphology for these nanoparticles. Combining advanced structure modelling, we demonstrated that the nanoparticles adopt an oblate shape with the minor-axis along the *b*-axis. For the CuF<sub>2</sub> conversion material, which theoretically has an exceptionally high specific energy density, behaves differently in practice when compared with other fluorides, such as FeF<sub>2</sub> and NiF<sub>2</sub>. The mechanism underlying its unique electrochemical performance and poor reversibility were investigated via a variety of characterization methods, including cyclic voltammetry (CV), X-ray absorption near edge structure (XANES), PDF and NMR spectroscopy. We demonstrated that Cu dissolution takes place upon charge, associated with the consumption of the LiF phase via the formation of a  $\mathrm{Cu}^{1+}$  intermediate. Such side reaction prevents  $\mathrm{Cu}$  from transforming back to  $\mathrm{CuF}_2$ , leading to negligible capacities in subsequent cycles and making this material challenging to use in a rechargeable battery.

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- 1. <u>X. Hua</u>, Z. Liu, P. G. Bruce and C. P. Grey, The Morphology of TiO<sub>2</sub> (B) Nanoparticles (in preparation).....basis of Chapter 4
- X. Hua, R. Robert, L. S. Du, K. M. Wiaderek, M. Leskes, K. W. Chapman, P. J. Chupas and C. P. Grey, Comprehensive Study of the CuF<sub>2</sub> Conversion Reaction Mechanism in a Lithium-ion Battery, *The Journal of Physical Chemistry C* 2014, *118* (28), 15169-15184 (ACS Editors' Choice, July 03, 2014).....basis of Chapter 5
- F. Pourpoint<sup>#</sup>, <u>X. Hua<sup>#</sup></u>, D. S. Middlemiss, P. Adamson, D. Wang, P. G. Bruce and C. P. Grey, New Insights into the Crystal and Electronic Structures of Li<sub>1+x</sub>V<sub>1-x</sub>O<sub>2</sub> from Solid State NMR, Pair Distribution Function Analyses, and First Principles Calculations, *Chemistry of Materials* 2012, *24*, 2880-2893 (authors contributed equally to this manuscript)......basis of Chapter 3
- Y. Y. Hu, Z. Liu, K. W. Nam, O. J. Borkiewicz, J. Cheng, <u>X. Hua</u>, M. T. Dunstan, X. Yu, K. M. Wiaderek, L. S. Du, K. W. Chapman, P. J. Chupas, X. Q. Yang and C. P. Grey, Origin of Additional Capacities in Metal Oxide Lithium-ion Battery Electrodes, *Nature Materials* 2013, *12*, 1130-1136.
- F. Wang, R. Robert, N. A. Chernova, N. Pereira, F. Omenya, F. Badway, <u>X. Hua</u>, M. Ruotolo, R. Zhang, L. Wu, V. Volkov, D. Su, B. Key, M. S. Whittingham, C. P. Grey, G. G. Amatucci, Y. Zhu and J. Graetz, Conversion Reaction Mechanisms in Lithium Ion Batteries: Study of the Binary Metal Fluoride Electrodes, *Journal of the American Chemical Society* 2011, 110925155717005.

## List of Abbreviations

2D	2-dimensional
3D	3-dimensional
APS	Advanced Photon Source
CCN-CuF <sub>2</sub>	carbon-coated nano-CuF2
СР	cross polarisation
DMC	dimethyl carbonate
DQ	double quantum
DW	Debye-Waller
EC	ethylene carbonate
EMC	ethyl methyl carbonate
EXAFS	extended X-ray absorption fine structure
fcc	face-centered cubic
FT	Fourier transform
FWHM	full width at half maximum
GITT	galvanostatic intermittent titration
HBM	high-energy ball milling
IB	integral breadth
JT	Jahn-Teller
LCA	linear combination analysis
LIB	lithium-ion battery
MAS	magic angle spinning
МСМ	mixed conductive matrix
Ni-Cd	nickel-cadmium
Ni-MH	nickel-metal hydride
NMP	N-methylpyrrolidinone
NSLS	National Synchrotron Light Source

PBM	planetary ball milling
PCA	principal component analysis
PDF	pair distribution function
PTFE	polytetrafluoroethylene
PVDF	polyvinylidenefluoride
RF	radiofrequency
SAXS	small-angle X-ray scattering
SEI	solid electrolyte interface
SQ	single quantum
SR	saturation recovery
TEM	transmission electron microscopy
TT	target transformation
XAFS	X-ray absorption fine structure
XANES	X-ray absorption near edge structure
XAS	X-ray absorption spectroscopy
XRD	X-ray diffraction
XRPD	X-ray powder diffraction

# List of Important Symbols

a	major radius of an ellipsoid
$B_0$	external magnetic field
В	atomic temperature factor (XRPD)
D	diameter of a particle
Ø	diameter
$D_{v}$	volume-weighted particle diameter
$E_0$	edge energy of X-ray absorption
$f_a(Q), f_a, f$	atomic scattering factor
$f_d(r)$	size distribution function
$f_e$	electron scattering length
F(Q)	particle structure factor
$\gamma_0(r)$	shape function
G(r)	pair distribution function
I(Q)	scattering intensity
$\mu(E)$	X-ray absorption coeffecient
N <sub>a</sub> , N	number of atoms
$N_{ab}$ , $N_p$	number of atom pairs
N <sub>e</sub>	number of electrons
Р	total scattered power of an electron
$P_a(r)$	Patterson function
Q	momentum transfer
$ ho_0$	average (atomic) number density
$ ho_{0e}$	average electron density
$\rho_a(r)$	atomic electron density
$ \rho_e(r) $	(individual) electron density
$ ho_p(r)$	pair density
R(r)	radial distribution function
$\rho(r)$	particle electron density
$\rho_t(r)$	particle atomic (number) density
$R_w$	agreement factor of the PDF refinement
$\bar{S}$	scattering vector
S(Q)	normalized scattering intensity
$S_i(Q)$	interference structure factor

$T_1$	spin-lattice relaxation time
τ	recovery time; delay time
$T_{ij}(r)$	atom distribution function (Gaussian)
U	atomic temperature factor (PDF)
υ	aspect ratio of an ellipsoid
V	volume of a particle
V(r)	volume correlation function
Ζ	atomic number, total number of electrons in an atom

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### **1** Introduction

#### 1.1 Primary and Secondary Batteries

From the moment when the first battery, the Voltaic pile, was invented by Alessandro Volta more than 200 years ago, we have witnessed a great revolution in battery science and technology, particularly since the late 20th century.



Figure 1.1 Diagram of a basic battery. Arrows suggest the flow direction of electrons (black), anions (red) and cations (green).

In general, batteries are chemical devices which convert chemical energy into electrical energy. A basic battery cell consists of two electrodes, separated by an ionically conductive, electronically insulating medium, known as electrolyte. It can either be a liquid or a solid. When the battery is connected with an external load, such as an electronic device (Figure 1.1), the redox reaction between the two electrodes is triggered. The negative electrode is oxidized providing a current of electrons, which flow through the load and are accepted by the positive electrode during the reduction reaction.

A battery can be categorised as either primary or secondary, based on the ability to reverse the redox reactions. Primary batteries appeared in the early stage of battery history and are expected to be disposed of after one discharge. Typical examples of primary batteries<sup>1</sup> are zinc-carbon and alkaline batteries. Secondary batteries, also known as rechargeable batteries, can be reused many times. The variation of the ability to recharge between different batteries originates from the reversibility of the redox reactions between the electrodes. A

reversible reaction allows the active materials to recover their original forms, which consequently allow the (secondary) battery to be recharged after use.

According to their chronological appearance, the most important secondary batteries are the lead-acid battery, the nickel-cadmium (Ni-Cd) / nickel-metal hydride (Ni-MH) battery, and the lithium-ion battery (LIB).<sup>2</sup> The comparison of their energy densities, shown in Figure 1.2, shows that the LIB has the highest energy density among the three types of batteries. The energy density, which reflects the energy storage capability, is known as the most basic and important criteria in the battery-screening process, along with the power density (W/kg or W/L).



Figure 1.2 Ragone plot: a comparison of the gravimetric (*x*-axis) and volumetric (*y*-axis) energy densities between different types of secondary batteries, adapted from an article published by Tarascon et al. in  $2001.^3$ 

Apart from a higher energy density compared to the lead-acid, Ni-Cd and Ni-MH batteries, LIBs have other advantages, such as high operating voltage, good low temperature performance, high rate capability and no memory effect, etc, which therefore leads to a wide application in the portable electronic devices. In addition, recent environmental concern such as the global warming and the finite nature of fossil fuels leads to the rise of LIBs in the automobile industry.<sup>3-4</sup>

#### **1.2 Lithium Ion Batteries**

#### 1.2.1 Conventional Lithium Ion Batteries

Figure 1.3 shows a diagram of the components in a commercial rechargeable LIB, which consists of graphite as anode and  $LiCoO_2$  for cathode, which both are insertion materials with layered structures. A separator is placed in the electrolyte in between the anode and cathode to avoid short circuit from direct contact of the two electrodes. Lithium ions move back and forth between the two electrodes during charge and discharge, obeying the chemical reactions:

cathode: 
$$\text{LiCoO}_2 \xrightarrow[dicharge]{charge} \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^-$$
 (1)

$$C_6 + xLi^+ + xe^- \xrightarrow[dicharge]{charge}{LiC_6} LiC_6$$
(2)

The process of lithium ions moving into the layered compound is called insertion, and the reverse process is named as extraction, also known as de-insertion.



Figure 1.3 Diagram of components in a conventional LIB comprised of graphite as an anode and a layered Li insertion material as a cathode. Arrows suggest the flow direction of the  $Li^+$  cations in the electrolyte and electrons in the circuit during charge (red) and discharge (green).

#### **1.2.2** First Generation of Insertion Materials

The outstanding capability of insertion materials to host Li in their framework structure gives rise to excellent cycleability and thus good capacity retention. The conventional insertion cathode compounds used in commercial LIBs, *i.e.*, LiCoO<sub>2</sub>, LiMn<sub>2</sub>O<sub>4</sub> and LiFePO<sub>4</sub>, are listed in the Table 1.1. Due to the intrinsic capacity limitation<sup>4</sup> upon (de)lithiation (discussed in 1.3.1), the actual capacities of these materials all fall in the range of 120 - 170 mAh/g, much smaller than the capacity of the graphite anode, 372 mAh/g. Therefore, in order to achieve a breakthrough in the storage capability for a full battery, the capacity restriction from these conventional insertion cathode materials has been generally considered as the primary

problem that needs to be solved. To this end, intensive research has been carried out in developing new cathode materials.

Material	erial LiCoO <sub>2</sub> LiMn <sub>2</sub> O <sub>4</sub> LiFePO <sub>4</sub>		LiFePO <sub>4</sub>	Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub>
Structure				· · · · · · · · · · · · · · · · · · ·
Electrode	+	+	+	-
Voltage (vs. Li <sup>+</sup> /Li) / V	3.0-4.4 <sup>5</sup>	3.5-4.3 <sup>6</sup>	3.4 <sup>7</sup>	1.55 <sup>8</sup>
Capacity* / mAh g <sup>-1</sup>	170 <sup>5</sup> (272 <sup>9</sup> )	120 <sup>4</sup> (148 <sup>6</sup> )	120-160 (170) <sup>7</sup>	150-160 (175) <sup>8</sup>
Energy Density* / Wh kg <sup>-1</sup>	250 (584) <sup>10</sup>	109 (392) <sup>10</sup>	156 (373) <sup>10</sup>	248 (271) <sup>8</sup>

Table 1.1 Comparison Between the Conventional Insertion Electrode Materials

\*: numbers in the brackets are theoretical values

Nevertheless, the negative aspects of using graphite as anode, *i.e.*, small volumetric capacity because of its low density<sup>11</sup> and slow rate performance due to the safety concern<sup>12</sup>, cannot be neglected. The safety concern of graphite under high rate arises from its low operating potential, which makes Li plating on graphite surface possible. When the charge current is very high, the Li keeps growing on the surface of graphite and forms dendrite, consequently leading to a short circuit and degradation of the battery's life. The alternative is the Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> anode, a zero-strain insertion compound which shows a remarkable cycleability with no SEI formation.<sup>8</sup> However, apart from its low capacity falling in the same range as those cathode materials (Table 1.1), the other downside of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> is the high reaction potential vs. Li<sup>+</sup>/Li, which leads to a low overall operating voltage in a full battery. These drawbacks of graphite and Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> anode materials.

#### **1.3** The Strategy for Developing Novel Materials

In this thesis, three strategies are proposed to develop novel materials, each followed by a case study which will be discussed in great detail in the later chapters.

#### 1.3.1 New Recipe: Composition

The energy density (Wh/kg) is given by the product of the specific capacity C (mAh/g) and the average operating potential E (V). Therefore, enhanced energy density can be achieved by either improving the specific capacity, or by increasing the operating potential.

In the literature, the capacity fading behavior for  $LiCoO_2$  has been mainly attributed to an ordering of Li ions and consequent structural distortions from hexagonal to monoclinic transformation<sup>13-14</sup>, coupled with Co dissolution at a voltage (vs.  $Li^+/Li$ ) > 4.2 V<sup>9, 15</sup>. In addition, the toxicity of Co has raised considerable environmental concern. The capacity fading in the LiMn<sub>2</sub>O<sub>4</sub> cathode is mainly ascribed to the difficulty in maintaining the structure integrity due to the symmetry reduction from the cubic Mn<sup>4+</sup>O<sub>6</sub> to the tetragonal Mn<sup>3+</sup>O<sub>6</sub> (Jahn-Teller (JT) distortion) upon discharge<sup>16</sup>, associated with the Mn dissolution at 4 V<sup>17</sup>.

These drawbacks have motivated the investigation of new materials:

1) layered or spinel  $Li_xM_yO_2$  compounds that are structurally analogous to  $LiCoO_2$  or  $LiMn_2O_4$ , including but not limited to:

a) isomorphic layered compounds<sup>18</sup>:

LiVO<sub>2</sub>, LiCrO<sub>2</sub>, LiNiO<sub>2</sub>, LiMnO<sub>2</sub>;

b) isomorphic spinels<sup>14</sup>:

 $LiTi_2O_4$ ,  $LiV_2O_4$ ;

2) surface modified LiCoO<sub>2</sub> using MgO or Al<sub>2</sub>O<sub>3</sub> as a coating material, which leads to a composition of LiM<sub>1-y</sub>Co<sub>y</sub>O<sub>2</sub> ( $M = Mg^{19}$ , Al<sup>20</sup>);

3) doped layered or spinel  $\text{Li}_{x}\text{M}_{y}\text{O}_{2}$  compounds, which results in a reduced concentration of either the toxic and high-cost Co or the JT-distorted  $\text{Mn}^{3+}$ . In addition, doping a proper element with a redox couple that has a high voltage versus Li helps to raise the operating potential, therefore enhancing the energy density.<sup>14</sup> The list below shows some doped variants of:

a) layered compounds:

LiNi<sub>1-y-z</sub>
$$Mn_yCo_zO_2^{21-22}$$
;

b) spinel compounds:

 $Li(Ti_{1.67}Li_{0.33})O_4 (= Li_4Ti_5O_{12})^8$ ,  $LiM_xMn_{2-x}O_4 (M = Li, Mg, Zn, Al, Ni, Cu, Co, Cr, Fe)^{23}$ . The doping strategy has also been applied to the olivine LiFePO<sub>4</sub>. Various studies show that doping Mn, Ni and Co in LiFePO<sub>4</sub> utilizes the redox couples such as  $Mn^{4+}/Mn^{3+}$ ,  $Ni^{3+}/Ni^{2+}$  and  $Co^{3+}/Co^{2+}$  that operate at a higher potential than  $Fe^{3+}/Fe^{2+}$ , thus leading to increased operating potentials for the doped variants of olivine LiM<sub>x</sub>Fe<sub>1-x</sub>PO<sub>4</sub>.<sup>24-25</sup>

In addition, due to a very stable  $(PO_4)^{3-}$  framework in LiFePO<sub>4</sub>, extensive efforts have been devoted to develop materials containing new polyanionic frameworks such as:

#### 1.3.1.1 Case Study: Li<sub>1+x</sub>V<sub>1-x</sub>O<sub>2</sub> as Anode

With respect to the alternative to graphite as an anode, oxide insertion compounds are attractive because their physical density is about twice that of graphite, leading to double the volumetric energy density. Among those oxide insertion hosts, LiVO<sub>2</sub> has drawn a lot of attention due to its low operating voltage of about 0.1 V, which is comparable to that for graphite. But the volumetric energy density of LiVO<sub>2</sub> is 1,360 mAh/cm<sup>3</sup> much higher than that of graphite, 790 mAh/cm<sup>3,11</sup> A recent study of the electrochemical performance of  $Li_{1+x}V_{1-x}O_2$  demonstrated that only Li-excess materials (x > 0) reached good capacities, with the best value achieved at the composition of  $Li_{1.07}V_{0.93}O_2$ . However, the lab X-ray powder diffraction (XRPD) of samples with various compositions yielded the same diffraction pattern, meaning the average structure is independent of the composition. This indicated that the local structure of  $Li_{1+x}V_{1-x}O_2$  governs the electrochemical behaviour, which motivated the current work to employ techniques for local structural characterization, *i.e.*, nuclear magnetic resonance (NMR) spectroscopy and pair distribution function (PDF) analyses. In Chapter 3, I will introduce the derivation of a structure model for the stoichiometric LiVO<sub>2</sub> sample, and the interpretation of the <sup>6</sup>Li NMR spectra (collected by my co-worker, Dr. Frédérique Pourpoint) using this model.

#### **1.3.2** New Architecture: Morphology

Instead of altering and/or tuning the chemical compositions (section 1.3.1), nanostructuring conventional and new electrode materials has drawn a growing interest for energy storage and conversion. Due to developments in structure engineering and materials manufacturing, nanostructured materials with various morphologies such as nanoparticles<sup>28</sup>, nanotubes<sup>29</sup>,

nanowires<sup>30</sup>, and materials with a more complex micro/nano-hierarchical structures<sup>31</sup> have been intensively studied in recent years and the investigation of their applications in LIBs has demonstrated a great potential in enhancing the electrochemical performance<sup>32-33</sup>.

The benefits of nanoscaling include, but are not limited to, i) a better accommodation of the strain due to Li (de)insertion, which leads to a higher capacity and better cycleability; ii) a larger interface for Li<sup>+</sup> incorporation and iii) a shorter path length for electronic/ionic transport arising from the increased surface area, which results in an improved rate capability.<sup>32-33</sup>

#### 1.3.2.1 Case Study: TiO<sub>2</sub>-B Nanoparticles as Anode

Apart from LiVO<sub>2</sub>, TiO<sub>2</sub> has also received a growing interest among the oxides due to its promising electrochemical performance compared to the carbon anode<sup>34</sup>: i) TiO<sub>2</sub> has a theoretical capacity comparable to that of graphite and as an oxide, it has twice the physical density of graphite, therefore twice the theoretical volumetric energy density; ii) the operating voltage of TiO<sub>2</sub> is around 1.5 V (vs. 0 V for graphite) and consequently is safer than graphite under high cycling rates. More importantly, the existence of various polymorphs of TiO<sub>2</sub> has spurred intensive research in its structure engineering. The best performance to date for TiO<sub>2</sub> has been found in the nanoparticlate bronze (B) phase with an average size of 3 nm, which retains good capacity at an exceptionally high cycling rate compared to its counterparts.<sup>35</sup> A recent morphology study of these TiO<sub>2</sub>-B nanoparticles using Debye refinement of the Bragg diffraction data indicated a prolate ellipsoid structure. However, the structural analysis of the nanosized material solely via XRPD is usually limited to the long-range order due to the nature of the diffraction technique, and challenged by the peak broadening due to the small particle sizes; the short-range structure that is sensitive to particle morphologies (see Figure 2.11) and often deviates from the average has been thus far overlooked. In Chapter 4, I will demonstrate our analyses employing small-angle X-ray scattering (SAXS) and PDF via advanced structure modelling, to provide a better description of the morphology for these nanoparticles.

#### 1.3.3 New System: Mechanism

#### **1.3.3.1** Conversion Materials

As discussed in section 1.3.1, the storage capacities of the conventional insertion materials, *i.e.*,  $LiCoO_2$  and  $LiMn_2O_4$ , are severely restricted by the requirement of functioning in the structure homogeneity range upon Li (de)insertion. However, the intrinsic capacity limitation

of these insertion materials (Table 1.1) originates from the reaction mechanism which is associated with  $\leq 1$  electron transfer per redox-active ion. Such restriction has fueled the exploration of functional materials operating via new routes.

A lot of effort has been recently focused on binary metal oxides and fluorides ( $M_aX_b$ , X = O, F), which operate via a conversion mechanism forming metal (M) and Li<sub>2</sub>O or LiF phases during discharge, and returning to the original  $M_aX_b$  phase upon charging:<sup>36</sup>

$$M_a X_b + nb \text{Li} \xrightarrow[charge]{discharge}{b \text{Li}_n X} + a M$$
(3)

Depending on the oxidation state of the metal ion, Li incorporation involves more than one electron transfer, which leads to much higher capacities than those observed for the conventional insertion compounds.<sup>36</sup> Table 1.2 shows the theoretical potentials, capacities and energy densities for various divalent *3d* transition-metal fluorides and oxides. The capacities for fluorides all fall in the range of 520 - 580 mAh g<sup>-1</sup>, and the values for oxides surpass 670 mAh g<sup>-1</sup>. In contrast to the capacities from insertion compounds (Table 1.1), these conversion materials show a great potential in improving the energy storage capability of the LIBs.

Table 1.2 Theoretical average potential, specific capacity and specific energy density for a variety of divalent 3d transition-metal fluorides and oxides, adapted from the article published by G. G. Amatucci et al. in 2007<sup>37</sup>

	fluorides MF <sub>2</sub>		oxides MO			
$\mathbf{M}\mathbf{X}_b$	V / E	Capacity / mAh g <sup>-1</sup>	Energy Density / Wh kg <sup>-1</sup>	V / E	Capacity / mAh g <sup>-1</sup>	Energy Density / Wh kg <sup>-1</sup>
$\mathbf{Mn}\mathbf{X}_b$	1.92	577	1108	1.03	756	779
$\mathbf{FeX}_b$	2.66	571	1519	1.61	746	1201
$\mathbf{Co}\mathbf{X}_b$	2.85	553	1578	1.80	715	1287
$\mathbf{NiX}_b$	2.96	554	1640	1.95	718	1400
$\mathbf{Cu}\mathbf{X}_b$	3.55	528	1874	2.25	674	1517

The theoretical capacity (gravimetric),  $C_{th}$  (mAh/g), is given by the following Equation<sup>38</sup>,

$$C_{th} = \frac{1000 \times n \times F}{3600 \times M} \tag{4}$$

where *n*, the number of electron transfer per redox-active ion, equals 2 for divalent metal compounds; *F* refers to Faraday constant which has a value of 96500 C/mol; and *M* is the molar mass of the compound. The theoretical potential,  $E_{th}$  (V), is calculated from the thermodynamic Equation via the Gibbs free energy,  $\Delta G^{\circ}$  (kJ/mol):

$$\Delta G^{\circ} = -nFE_{th} \tag{5}$$

where *n* and *F* have the same definitions as those in Equation 4; the  $\triangle G^{\circ}$  for reaction 3 is related to the standard Gibbs free energy of the specific compound as follows:

$$\Delta G^{\circ} = b \times \Delta G^{\circ}_{Li_n X} - \Delta G^{\circ}_{M X_b} \tag{6}$$

the values for  $\Delta G_{Li_nX}^{\circ}$  and  $\Delta G_{MX_b}^{\circ}$  can be obtained from the table of thermodynamics quantities<sup>39</sup>. Finally the theoretical specific energy density (Wh/kg) is given by the product of the theoretical specific capacity ( $C_{th}$ ) and theoretical operating potential ( $E_{th}$ ).

#### **1.3.3.2** Case Study: CuF<sub>2</sub> as Cathode

In the search for alternatives to the conventional insertion cathode materials, the 3d transitionmetal fluorides  $(MF_x)$  have received the most interest due to their ability to deliver high electrochemical energy density, mainly due to their high theoretical potentials (Table 1.2) which arise from the fluorides' high Gibbs free energy of formation.<sup>37</sup> Among those fluorides, CuF<sub>2</sub> stands out as a very promising candidate due to its high specific capacity of 528 mAh/g (from Equation 4 with  $M_{CuF2} = 101.54$  g/mol) and the highest theoretical potential of 3.55 V (from Equation 5 and 6 using the  $\triangle G_{\text{LiF}}^{\circ}$  and  $\triangle G_{\text{CuF}_2}^{\circ}$  obtained from the table of thermodynamics quantities<sup>39</sup>, which equal -616.93 and -548.94 kJ/mol, respectively) among all the divalent 3d transition-metal fluorides, leading to an exceptionally high energy density of 1874 Wh/kg.<sup>37,40</sup> However, the electrochemical performance of CuF<sub>2</sub> is drastically different in practice. Its sensitivity to moisture engenders a significant challenge for material preparation and electrode fabrication. The intrinsically large band gap, arising from the high electronegativity of fluorine, makes CuF<sub>2</sub> a poor electronic conductor. Although nanosizing and embedding the materials into a carbon matrix<sup>41</sup> has demonstrated full utilization of the theoretical capacity of CuF<sub>2</sub> in the first discharge, as well as an increase of operating potential to 3 V, in contrast to other fluorides, such as FeF<sub>2</sub> and NiF<sub>2</sub>, good capacity retention has not yet been achieved for CuF<sub>2</sub>. The reaction mechanisms that occur in the 1st and subsequent cycles and the reasons for the poor charging performance of  $CuF_2$  were studied (Chapter 5) via a variety of characterisation methods, including; cyclic voltammetry (CV), X-ray absorption near edge structure (XANES), PDF and NMR.
# 2 X-ray Investigation and Other Techniques

X-rays are a form of electromagnetic radiation, with a wavelength in the range of 0.01 - 100 Å<sup>42</sup>. Since it was discovered more than 100 years ago, it has revolutionized many areas of modern science and technology. In the materials and crystallographic sciences, X-ray-related techniques have become an essential tool to probe the structure of materials with dimensions from the macro to the nano scale. Therefore, in this chapter, X-ray related techniques will be discussed in great detail, with the other important techniques introduced in the latter part.

# 2.1 X-ray Scattering

When a monochromatic X-ray beam hits a sample, the phenomenon involves two interactions: scattering and absorption (Section 2.2).

# 2.1.1 Scattering by an Electron

In the scattering process, the incident photon beam can be deflected with or without an energy loss.

# 2.1.1.1 Compton Scattering



Figure 2.1 Diagram of (a) the X-ray scattering process and (b) the law of the momentum conservation. The black dot in (a) denotes an electron; blue solid arrows represent the incident waves; red solid arrows are the scattered waves; black arrow in (a) refers to the recoil electron, while the one in (b) illustrates the momentum transfer.  $2\theta$  is the angle between the incident and the scattered waves.

If the scattering involves an energy loss, the scattered radiation will have a slightly larger wavelength than the incident beam and such inelastic scattering process is defined as Compton scattering. The amount of wavelength change  $d\lambda$  is called the Compton shift.<sup>43</sup>

Assuming photon beam I hits an electron at point O in an irregular object shown in Figure 2.1a, this gives rise to a scattered beam with a recoil electron. From the conservation of energy in the elastic collision, we have that

$$\frac{hc}{\lambda} = \frac{hc}{\lambda + d\lambda} + \frac{1}{2}mv^2.$$
(7)

The left part of this equation is the energy of the incident photon with a wavelength of  $\lambda$ , where *h* is Planck's constant and *c* refers to the speed of light; the right part comprises the energy of the deflected photon with a wavelength of  $\lambda + d\lambda$  and the energy of the recoil electron,  $\frac{1}{2}mv^2$ , where  $d\lambda$  corresponds to the wavelength change, known as the Compton shift and *m* and *v* are the mass and the speed of the recoil electron. Moving the energies of both the incident and deflected beam to the same side yields,

$$\frac{hc}{\lambda} - \frac{hc}{\lambda + d\lambda} = \frac{1}{2}mv^{2}$$

$$\implies \frac{hc \cdot d\lambda}{\lambda(\lambda + d\lambda)} = \frac{1}{2}mv^{2}.$$
(8)

Finally we have the approximation,

$$\frac{hc}{\lambda^2} \cdot d\lambda = \frac{1}{2}mv^2. \tag{9}$$

According to the diagram illustrated in Figure 2.1b, the momentum of the scattered photon and recoil electron should obey the law of momentum conservation. Considering it is a valid approximation to ignore the change of the momentum magnitude of the scattered photon<sup>43</sup>, hence from the geometry of the scattering, we can deduce

$$\frac{h}{\lambda}\sin\theta = \frac{1}{2}m\nu,\tag{10}$$

where  $\theta$  is the scattering angle. Thus the change of the wavelength (Compton shift),  $d\lambda$ , can be obtained by combining Equations 9 and 10 together,

$$d\lambda = \frac{h}{mc}(1 - \cos 2\theta) = 0.024 \cdot (1 - \cos 2\theta) \,(\text{Å}). \tag{11}$$

From Equation 11, we can conclude that the Compton shift is independent of the wavelength of the incident beam and only depends on the scattering angle. A plot of this relation is illustrated in Figure 2.2, where  $d\lambda$  is very small at low scattering angle and gets more pronounced as the angle increases. It finally reaches maximum of 0.048 Å at a 2  $\theta$  of 180° (backscattering<sup>44</sup>).



Figure 2.2 Illustration of the relation between the scattering angle and the Compton shift, based on Equation 11.

The significance of these observations is reflected in small-angle (Section 2.1.5) and total (Section 2.1.7) scattering experiments, where the Compton scattering can be ignored at low angle. However, a wavelength correction needs to be implemented in the analysis of the PDF data via the total (wide-angle) scattering experiment.

# 2.1.1.2 Thomson Scattering



Figure 2.3 Diagram of (a) Thomson scattering in an orthogonal coordinate and (b) solid angle  $d\Omega$  in a spherical coordinate system<sup>44</sup>. Blue and red arrows represent the incident (subscript I) and scattered (subscript D) beam, respectively (adapted from the reference<sup>44</sup>);  $\overline{E}$  refers to the electric field of the electromagnetic wave; subscripts  $\perp$  and  $\parallel$  imply the vertical and horizontal components of the corresponding  $\overline{E}$  relative to the *xz*-plane, respectively.  $2\theta$  is the scattering angle.  $\phi$  is the angle between the direction of the incident  $\overline{E}$  and the direction of the scattered beam.

If the incident photons are deflected without a loss of energy, the scattered radiation is expected to have the same radiation wavelength as the incident and this elastic coherent scattering process is named after J. J. Thomson.<sup>43-44</sup> X-ray crystallography is developed on the basis of Thomson scattering, which is the foundation for the three main scattering techniques: small-angle scattering (Section 2.1.5), diffraction (Section 2.1.6) and PDF (Section 2.1.7).

As illustrated in Figure 2.3a, when a monochromatic incident beam I with a frequency of v and an electric vector  $\overline{E}_{I}$  hits an electron with a mass of m and charge of e placed at position O, the electromagnetic wave I exerts a periodic force  $\overline{F} = e \overline{E}_{0I}$  on the electron. Therefore, the electron experiences oscillatory motion with acceleration. According to the classical electromagnetic theory<sup>43</sup>, an accelerating particle emits electromagnetic waves, D in Figure 2.3a. For this reason, Thomson scattering can be understood as a process involving absorption and re-emission of radiation.

If  $\overline{E}_D$  is the electric field vector for the emitted (deflected) electromagnetic wave D at position P with a distance *r* away from the scatterer, the electric field of  $\overline{E}_D$  can be described as

$$\bar{E}_D = \bar{E}_{0D} \cdot e^{2\pi i \nu \left(t - \frac{r}{c}\right) - i\alpha},\tag{12}$$

where *t* is the time and  $\alpha$  corresponds to the phase lag due to the absorption-emission process. According to Thomson, the scattering of a free electron is coherent and there is a well-defined phase relation between the incident and the scattered radiation,  $\alpha = \pi$ .<sup>44</sup> Apart from  $\alpha$ , the distance *r* also introduces a phase shift of  $-2\pi rv/c$ . Hence, the exponential part in Equation 12 can be described as the phase correction. Concerning the  $\overline{E}_{0D}$ , Thomson concluded that it has the following relation with the incident wave  $\overline{E}_{0I}$ ,

$$\bar{E}_{0D} = \frac{1}{r} \cdot \frac{e^2}{m_e c^2} \cdot \bar{E}_{0I} \sin \phi, \qquad (13)$$

where  $\phi$  is the angle between the direction of the acceleration of the electron and the direction of the scattered wave (usually defined as the direction of our observation in some textbooks<sup>43-</sup> <sup>44</sup>). It reveals the decrease of the amplitude of  $\overline{E}_{0D}$  is inversely proportional to the distance r, which is caused by scattering of radiation in all directions<sup>44</sup>. Therefore Equation 13 can be understood as the amplitude correction. From it, we can then deduce the intensity relation:

$$I_{0D} = \frac{1}{r^2} \cdot \frac{e^4}{m_e^2 c^4} \cdot I_{0I} \sin^2 \phi.$$
(14)

The electric vectors for both incident wave  $\overline{E}_{I}$  and scattered wave  $\overline{E}_{D}$  can be decomposed into two vectors with one  $\overline{E}_{\perp}$  perpendicular and the other  $\overline{E}_{\parallel}$  parallel to the plane which contains the incident and scattered beam, as the *xz*-plane in Figure 2.3a. The geometry of this example gives rise to relations:  $\overline{E}_{0D\perp} = \overline{E}_{0I\perp}$  and  $\overline{E}_{0D\parallel} = \overline{E}_{0I\parallel} \cos 2\theta$ , where  $2\theta$  is the scattering angle. When the incident beam is completely polarized along the *y*-axis,  $\phi = 90^{\circ}$  which leads to

$$I_{0D} = \frac{1}{r^2} \cdot \frac{e^4}{m_e^2 c^4} \cdot I_{0I}.$$
 (15)

However, when the incident beam is completely polarized along the *z*-axis,  $\phi = 90^{\circ}-2\theta$  which results in

$$I_{0D}(\theta) = \frac{1}{r^2} \cdot \frac{e^4}{m_e^2 c^4} \cdot I_{0I} \cdot \cos^2 2\theta.$$
(16)

In a general case, if the intensity percentage of  $\overline{E}_{0I}$  and  $\overline{E}_{0I}$  is  $f \perp$  and  $f_{\parallel}$  respectively, we then have

$$I_{0D}(\theta) = \frac{1}{r^2} \cdot \frac{e^4}{m_e^2 c^4} \cdot I_{0I} \left( f_{\perp} + f_{\parallel} \cos^2 2\theta \right).$$
(17)

If both  $f \perp$  and  $f \parallel$  equal 0.5, Equation 17 becomes

$$I_{0D}(\theta) = \frac{1}{r^2} \cdot \frac{e^4}{m_e^2 c^4} \cdot I_{0I} \frac{1 + \cos^2 2\theta}{2}.$$
 (18)

Term  $(1 + \cos^2 2\theta)/2$  is called the polarisation factor<sup>44</sup>, which indicates that the scattered radiation achieves the maximum intensity in the direction of the incident beam (along *x*-axis in Figure 2.3a), while the minium occurs in the direction perpendicular to the direction of the incident beam (on the *yz*-plane).

#### 2.1.1.3 (Thomson) Electron Scattering Length

Equation 18 gives the intensity scattered into a solid angle  $d\Omega$  at  $2\theta$ . From Figure 2.3b, we can derive

$$d\Omega = 2\pi \cdot r \sin 2\theta \cdot r d(2\theta). \tag{19}$$

The total scattered power of an electron<sup>43-44</sup>, *P*, can be obtained by the integration of Equation 18 from 0 to  $\pi$ , which is given by

$$P = \int_{0}^{\pi} I_{0D} d\Omega = I_{0I} \frac{e^{4}}{m_{e}^{2} r^{2} c^{4}} \cdot \int_{0}^{\pi} \frac{1 + \cos^{2} 2\theta}{2} 2\pi r^{2} \sin 2\theta \, d(2\theta)$$
  
$$= \frac{8\pi e^{4}}{3m_{e}^{2} c^{4}} I_{0I} = \frac{8\pi r_{e}^{2}}{3} I_{0I}.$$
 (20)

where term  $e^2/(m_ec^2)$  is usually defined as  $r_e$ , the (Thomson) scattering length or classical electron radius, which is equal to  $2.8 \times 10^{-13}$  cm.<sup>43</sup>

If we combine the amplitude and phase correction from Equation 12 and 13 together, the scattering amplitude from a single electron can be obtained:

$$E_D = \frac{1}{r} \cdot \frac{e^2}{m_e c^2} \cdot E_{0I} \sin \phi \ e^{2\pi i \nu \left(t - \frac{r}{c}\right) - i\alpha}.$$
(21)

The Thomson scattering length  $e^2/(mc^2)$  is a constant for electron scattering. The term  $\sin \phi$  was described as the polarisation factor in Section 2.1.1.2, and can be given by a cosine function of  $2\theta$  when the polarisation of the incident beam is known. Hence, for simplification, term  $e^2/mc^2 \cdot \sin \phi$  will be replaced by  $f_e$ :

$$f_e = \frac{e^2}{m_e c^2} \sin \phi, \qquad (22)$$

which contains the polarisation term, and is a function of scattering angle  $2\theta$  (Equation 18).

In addition, the amplitude of scattered beam at position P,  $E_D$  and the amplitude of the incident wave  $E_{0I}$  will be both simplified as E and  $E_0$ , respectively. Hence the final scattering amplitude function can be rewritten as follows:

$$E(r,t) = f_e \frac{E_0}{r} \cdot e^{2\pi i \nu \left(t - \frac{r}{c}\right) - i\alpha}$$
(23)

where the left part  $f_e E_0/r$  describes the amplitude change, while the exponential function on the right corresponds to the phase correction.

# 2.1.2 Scattering by a Set of Electrons (Atom)

#### 2.1.2.1 Interference and Momentum Transfer

In the event of wave scattered by a pair of electrons (Figure 2.4a), two parallel beam  $I_1$  and  $I_2$  collides with two electrons at positions  $O_1$  and  $O_2$ , respectively. Assuming point P is at the position with an indefinitely large distance relative to the distance between the pair of electrons ( $O_1P \gg O_1O_2$ ), hence i) the scattering angles for both incident beams can be

considered as  $2\theta$ ; ii)  $O_1P \approx O_2P$ , leading to the same amplitude part  $f_e E_0/r$  in the scattering amplitude functions (Equation 23) for two scattered waves  $D_1$  and  $D_2$ .



Figure 2.4 (a) Diagram of parallel waves ( $I_1$  and  $I_2$ ) scattered by a pair of electrons ( $O_1$  and  $O_2$ ) at a scattering angle  $2\theta$ . The scattered waves  $D_1$  and  $D_2$  converge at point P; (b) diagram of the geometry of the scattering vectors.

We can define  $\overline{S}_{I}$  and  $\overline{S}_{D}$  as the unit vectors along the direction of incident and scattered waves respectively, and  $\overline{r} = \overline{O_1 O_2}$ . The phase difference between the two scattered waves can be calculated based on simple geometry illustrated in Figure 2.4a:

$$\begin{aligned} \alpha_{O_1O_2} &= -\frac{2\pi}{\lambda} \left( CO_2 + O_2 G \right) \\ &= -\frac{2\pi}{\lambda} \left( \bar{r} \cdot \bar{S}_I - \bar{r} \cdot \bar{S}_D \right) \\ &= 2\pi \bar{r} \frac{(\bar{S}_D - \bar{S}_I)}{\lambda}. \end{aligned}$$
(24)

From Figure 2.4b, we can deduce:

$$\bar{s} = \frac{\overline{S_D} - \overline{S_I}}{\lambda}, \qquad s = \frac{2\sin\theta}{\lambda}.$$
 (25)

If  $(\overline{S_D} - \overline{S_I})/\lambda$  in Equation 24 is replaced with  $\overline{s}$ , we can obtain the final phase shift,

$$\begin{aligned} \alpha_{O_1 O_2} &= 2\pi \bar{r} \cdot \bar{s} \\ &= \bar{O} \bar{r}, \end{aligned} \tag{26}$$

where  $\bar{Q} = 2\pi \bar{s}$  is defined as the momentum transfer, meaning the amount of momentum that one particle (the photon in this example) gives to another particle (electron in this example). The magnitude of this has the expression:

$$Q = \frac{4\pi \sin \theta}{\lambda}.$$
 (27)

According to this relation, we know that a larger scattering angle  $\theta$  corresponds to a larger Q.

#### 2.1.2.2 Atomic Scattering Factor

With regard to the amplitude part of the scattering wave function, they have a form of  $f_e E_0/r$  for wave D<sub>1</sub> and D<sub>2</sub>. The only difference arises from the phase shift  $\alpha_{O_1O_2}$  due to the momentum transfer. Therefore, the resultant amplitude of the scattering waves at point P can be written as

$$E_{p}(r,t) = f_{e} \frac{E_{0}}{r} \cdot \left[ \left( e^{2\pi i \nu \left( t - \frac{r}{c} \right) - i\alpha} \right) + \left( e^{2\pi i \nu \left( t - \frac{r}{c} \right) - i\alpha + i\bar{Q}\bar{r}} \right) \right]$$
  
$$= f_{e} (1 + e^{i\bar{Q}\bar{r}}) \frac{E_{0}}{r} \cdot e^{2\pi i \nu \left( t - \frac{r}{c} \right) - i\alpha},$$
(28)

with the new amplitude part modified as

$$f(\bar{Q}) = f_e \cdot (1 + e^{iQ\bar{r}}). \tag{29}$$

Equation 29 can be extended to a general case where the beam is scattered by an atom with an ensemble of electrons. The resulting amplitude part then becomes the atomic scattering factor,

$$f_a(\bar{Q}) = \sum_j^z f_e \cdot e^{i\bar{Q}\bar{r}_j}$$
(30)

For convenience, Equation 30 is usually rewritten in a spherical coordinate system using the atomic electron density  $\rho_a(\bar{r})$ , which is the sum of the individual electron densities  $\rho_e(\bar{r})$ :

$$\rho_{a}(\bar{r}) = \sum_{j=1}^{z} \rho_{ej}(\bar{r}).$$
(31)

Thus the atomic scattering factor becomes

$$f_a(\bar{Q}) = f_e \int_{\nu} \rho_a(\bar{r}) e^{i\bar{Q}\bar{r}} d\bar{r}.$$
(32)

Because the X-ray scattering is mainly contributed to the strongly bound electrons in the lower and fully occupied electron orbitals, the atomic electron density  $\rho_a(\bar{r})$  can be considered as spherically symmetric.<sup>45</sup> Hence, Equation 32 can be simplified as

$$f_a(Q) = f_e \int_{\nu} \rho_a(r) e^{i\bar{Q}\bar{r}} d\bar{r}.$$
(33)

To perform the integration over the whole volume, it is important to understand the meaning of a volume element in a spherical coordinate system, which is the grey area illustrated in Figure 2.5. It can be computed from

$$\int_{v} d\bar{r} = \iiint r \sin \varphi d\theta \cdot r d\varphi \cdot dr$$

$$= \int_{0}^{2\pi} d\theta \iint r^{2} \sin \varphi d\varphi dr$$

$$= 2\pi \iint r^{2} \sin \varphi d\varphi dr,$$
(34)

where  $\varphi$  is the angle between  $\overline{Q}$  and  $\overline{r}$ , which falls in the range of  $0 - \pi$ , resulting in  $e^{i\overline{Q}\overline{r}} = e^{iQr\cos\varphi}$ . Therefore Equation 33 can be further rewritten using all scalar quantities:

$$f_{a}(Q) = 2\pi f_{e} \int \rho_{a}(r) r^{2} \int_{0}^{\pi} e^{iQr\cos\varphi} \sin\varphi \,d\varphi \,dr$$

$$= 4\pi f_{e} \int \rho_{a}(r) r^{2} \frac{\sin(Qr)}{Qr} dr.$$
(35)



Figure 2.5 Illustration of a volume element in a spherical coordinate system (adapted from the reference<sup>43</sup>).

Further calculation of the atomic scattering factor f requires knowledge of the electron density distribution function  $\rho_e(r)$ .<sup>45</sup> In general case,  $Q^{-1}$  is much larger than the atomic radius. Hence,  $Qr \ll 1$ , leading to term  $\sin(Qr)/Qr \approx 1$ . Then

$$f_a = 4\pi f_e \int \rho_a(r) r^2 \, dr. \tag{36}$$

Taking into account that the term  $4\pi r^2 \rho_a(r)$  is the atomic electron density at distance *r*, we derive  $4\pi \int \rho_a(r)r^2 dr = Z$ , which is the effective number of electrons. Finally, we can obtain the final simplified atomic scattering factor, <sup>44-45</sup>

$$f_a = \sum_{j=1}^{Z} f_{e_j} = Z f_e.$$
 (37)

It shows that  $f_a$  is proportional to the number of electrons in the atom.

# 2.1.3 Scattering by a Set of Atoms (Crystal)

# 2.1.3.1 Structure Factor

If  $\rho_{aj}(\bar{r})$  is the electron density of the *j*th atom at position of the origin, this atom at position  $\bar{r}_j$  (relative to the origin) will then have an atomic electron density  $\rho_{aj}(\bar{r} - \bar{r}_j)$ . Therefore, the electron density of a system  $\rho(\bar{r})$  containing *N* atoms is the sum over the individual electron density of each atom (similar to Equation 31),

$$\rho(\overline{r}) = \sum_{j=1}^{N} \rho_{aj} (\overline{r} - \overline{r_j}).$$
(38)

The amplitude of the scattered waves by these atoms then can be written as<sup>44</sup>

$$F(\bar{Q}) = f_e \int_{\nu} \rho(\bar{r}) e^{i\bar{Q}\bar{r}} d\bar{r}$$
(39)

$$= f_e \int_{\nu} \sum_{j=1}^{N} \rho_{aj} (\bar{r} - \bar{r}_j) e^{i\bar{Q}\bar{r}} d\bar{r}$$

$$\tag{40}$$

$$= f_e \sum_{j=1}^{N} \int_{v} \rho_{aj}(\overline{R_j}) e^{i\overline{Q}(\overline{r_j} + \overline{R_j})} d\overline{R_j}$$
$$= \sum_{i=1}^{N} \left[ f_e \int_{v} \rho_{zi}(\overline{R_i}) e^{i\overline{Q}\overline{R_j}} d\overline{R_i} \right] e^{i\overline{Q}\overline{r_j}}.$$
(41)

$$=\sum_{j=1}^{N}\left[f_{e}\int_{v}\rho_{aj}(\bar{R}_{j})e^{i\bar{Q}\bar{R}_{j}}d\bar{R}_{j}\right]e^{i\bar{Q}\bar{r}_{j}}.$$
(41)

The part in the square brackets corresponds to the atomic scattering factor  $f_{aj}(\bar{Q})$  of the *j*th atom and can be replaced with Equation 32. The resulting amplitude has a form similar to this  $f_a(\bar{Q})$  (Equation 30), and is called the structure factor:

$$F(\bar{Q}) = \sum_{j=1}^{N_a} f_{aj}(\bar{Q}) \cdot e^{i\bar{Q}\bar{r}_j}.$$
(42)

If we assume the electron density of the unit cell  $\rho(\bar{r})$  is spherically symmetric, we are able to convert Equation 39 into a form using spherical coordinates, in the same manner as the deduction of Equation 35 to derive,

$$F(Q) = 4\pi f_e \int \rho(r) r^2 \frac{\sin(Qr)}{Qr} dr.$$
(43)

#### 2.1.3.2 Structure Factor for an Isotropic Sphere

In an isotropic spherical particle, the *r*-dependent electron density  $\rho(r)$  can be replaced by the average electron density  $\rho_{0e} = N_e/V$ , where  $N_e$  is the number of electrons within the particle with a volume of *V*. Then Equation 43 becomes:

$$F(Q) = 4\pi f_e \int_0^R \rho_{0e} r^2 \frac{\sin(Qr)}{Qr} dr$$

$$= 4\pi \rho_{0e} f_e \int_0^{QR} \frac{\sin(QR)}{QR} \frac{(QR)^2}{Q^2} \frac{d(QR)}{Q},$$
(44)

where R is the radius of the sphere. To simplify the integration, we can replace QR with x,

$$F(Q) = 4\pi\rho_{0e}f_e \int_0^{QR} \frac{\sin x}{x} \frac{x^2}{Q^2} \frac{dx}{Q}$$
  
=  $4\pi\rho_{0e}f_e \frac{\sin(QR) - QR\cos(QR)}{Q^3}$   
$$\xrightarrow{\rho_{0e}=N_e/V} = \frac{4\pi N_e}{V} f_e \frac{\sin(QR) - QR\cos(QR)}{Q^3}$$
  
=  $\frac{4\pi N_e}{4\pi R^3/3} f_e \frac{\sin(QR) - QR\cos(QR)}{Q^3}$   
=  $3\rho_{0e}V f_e \frac{\sin(QR) - QR\cos(QR)}{(QR)^3}$ . (45)

The significance of this formula lies in the final equation used for data fitting in SAXS analysis, which will be introduced in Section 2.1.5.3.

# 2.1.3.3 Atomic Temperature Factor

In practice, atoms in a crystal experience vibrations mostly due to thermal motion. Hence an approximation needs to be incorporated into the structure factor  $F(\bar{Q})$  when the thermal deviation of the atomic position is important. Such approximation is called the Debye-Waller (DW) approximation, where a term describing the average deviation,  $\bar{u}$ , is added into position of the atom,  $\bar{R} = \bar{r} + \bar{u}$ .<sup>46</sup> Hence the exponential part in Equation 42 becomes,

$$e^{i\bar{Q}\bar{R}} = e^{i\bar{Q}(\bar{r}+\bar{u})} = e^{i\bar{Q}\bar{r}} \cdot e^{i\bar{Q}\bar{u}}$$
$$= e^{i\bar{Q}\bar{r}} \cdot \left[1 + i\bar{Q}\bar{u} - \frac{(\bar{Q}\bar{u})^2}{2} + \cdots\right].$$
(46)

The part in the square brackets is a Taylor series expansion of the exponential  $e^{i\bar{Q}\bar{u}}$ . Considering *u* is very small, and the mean of  $\bar{Q}\bar{u}$  equals zero, the Taylor series expansion can be reasonably simplified as  $1 - \frac{(\bar{Q}\bar{u})^2}{2}$ , which approximates the expansion of term  $e^{-\frac{1}{2}Q^2U}$ , where  $U = u^2$ . This exponential term  $e^{-\frac{1}{2}Q^2U}$  is called the Debye-Waller (DW) factor.

To take the thermal motions into account, we can implement the structure factor with the DW factor,

$$F(\bar{Q}) = \sum_{j=1}^{n} f_{aj}(\bar{Q}) \cdot e^{i\bar{Q}\bar{r}_j} \cdot e^{-\frac{1}{2}Q^2U}$$

$$\tag{47}$$

or

$$F(\bar{Q}) = \sum_{j=1}^{n} f_{aj}(\bar{Q}) \cdot e^{i\bar{Q}\bar{r}_{j}} \cdot e^{-\frac{1}{4}BQ^{2}},$$
(48)

where *B* and *U* are both the atomic temperature factors. *B* is commonly used in X-ray diffraction<sup>44</sup>, while *U* is preferably to be used by the X-ray pair distribution functions (PDF) community.<sup>46</sup> They are interchangeable via the following relation:

$$B = 8\pi^2 U (\mathring{A}^2). \tag{49}$$

#### 2.1.4 Intensity of Scattered Waves

In practice, the total intensity of the scattered waves has contributions from several parts<sup>46</sup>: i) coherent scattering, arising from Thomson scattering (Section 2.1.1.2) which has a dominant contribution to the whole intensity; ii) incoherent scattering, due to Compton scattering (Section 2.1.1.1), only significant at high scattering angle; iii) multiple-scattering, which occurs mainly within the sample; and iv) background scattering, which comes from the background component of the experiment excluding the sample, such as the sample holder.

Because the structural information is contained in the coherent scattering, therefore the discussion will be focused on Thomson scattering intensity,  $I(\overline{Q})$ .

The  $I(\overline{Q})$  is given by the absolute square of structure factor  $F(\overline{Q})$ , which can be obtained by the product of the  $F(\overline{Q})$  and its conjugate  $F^*(\overline{Q})$ .<sup>47</sup>

$$I(\overline{Q}) = |F(\overline{Q})|^2 = F(\overline{Q}) \cdot F^*(\overline{Q}).$$
<sup>(50)</sup>

## 2.1.4.1 Debye Equation

If we replace  $F(\overline{Q})$  in Equation 50 with Equation 42,

$$I(\bar{Q}) = \sum_{i=1}^{n} f_{ai}(\bar{Q}) \cdot e^{i\bar{Q}\bar{r}_{i}} \cdot \sum_{j=1}^{n} f_{aj}(\bar{Q}) \cdot e^{-i\bar{Q}\bar{r}_{j}}$$

$$= \sum_{i=j}^{n} f_{aj}^{2}(\bar{Q}) + \sum_{i}^{n} \sum_{j,i\neq j}^{n} f_{ai}(\bar{Q})f_{aj}(\bar{Q}) \cdot e^{i\bar{Q}(\bar{r}_{i}-\bar{r}_{j})}.$$
(51)

For simplification, let  $\overline{r_i} - \overline{r_j}$  be  $\overline{r_{ij}}$ . Therefore, the integration of  $e^{i\overline{Q}\overline{r_{ij}}}$  over all directions needs to be evaluated. Assuming the system is centrosymmetric, the summation of the  $e^{i\overline{Q}\overline{r_{ij}}}$ from two centrosymmetric positions, written in a complex form, leads to the imaginary parts (sine function) cancelling each other out. Therefore, to sum  $e^{i\overline{Q}\overline{r_{ij}}}$  over all positions is equivalent to average the real part of its complex form,  $\cos(\overline{Q}\overline{r_{ij}})$ , over all orientations:

$$\langle e^{i\bar{Q}\overline{r_{ij}}} \rangle = \langle \cos \overline{Q}\overline{r_{ij}} \rangle$$

$$= \int_0^{\pi} \cos(Qr_{ij}\cos\varphi) \frac{\sin\varphi}{2} d\varphi$$

$$= \frac{\sin(Qr_{ij})}{Qr_{ij}},$$
(52)

where  $\varphi$  is the angle between  $\overline{Q}$  and  $\overline{r}$  (Figure 2.5), and  $(\sin \varphi \, d\varphi)/2$  represents the probability of the angle falling in the range of  $(\varphi, \varphi + d\varphi)$ .<sup>48-49</sup> Finally, we obtain

$$I(Q) = \sum_{i=j}^{N} f_{aj}^{2} + \sum_{i}^{N} \sum_{j,i\neq j}^{N} f_{ai} f_{aj} \frac{\sin(Qr_{ij})}{Qr_{ij}}$$
(53)

$$=\sum_{i}^{N}\sum_{j}^{N}f_{ai}f_{aj}\frac{\sin(Qr_{ij})}{Qr_{ij}},$$
(54)

which is the equation first derived by Debye<sup>50</sup>. Both of these two forms (Equation 53 and 54) are commonly seen in literature and will be used later to calculate the X-ray diffraction intensities for small particles (Section 2.1.6.4).

## 2.1.4.2 Patterson Function

If we substitute  $F(\bar{Q})$  using Equation 39, we can derive

$$I(\bar{Q}) = f_e^2 \int_{\nu} \rho(\bar{u}) e^{i\bar{Q}\bar{u}} d\bar{u} \cdot \int_{\nu} \rho(\bar{r}') e^{-i\bar{Q}\bar{r}'} d\bar{r}'$$

$$= f_e^2 \iint_{\nu} \rho(\bar{u}) \rho(\bar{r}') e^{i\bar{Q}(\bar{u}-\bar{r}')} d\bar{u} d\bar{r}'$$

$$\xrightarrow{\bar{r}=\bar{u}-\bar{r}'} = f_e^2 \iint_{\nu} \rho(\bar{r}+\bar{r}') \rho(\bar{r}') e^{i\bar{Q}\bar{r}} d\bar{r} d\bar{r}'.$$
(55)

The integration  $\int \rho(\bar{r} + \bar{r}')\rho(\bar{r}')d\bar{r}'$  is the Patterson function:

$$P_a(\bar{r}) = \int_{\nu} \rho(\bar{r} + \bar{r}')\rho(\bar{r}')d\bar{r}' = \tilde{\rho}^2(\bar{r}), \qquad (56)$$

which summarizes all pairs with equal relative distance  $\bar{r}$ , and  $\tilde{\rho}^2(\bar{r})$  denotes the convolution square (self-correlation function) of the density  $\rho(\bar{r})$ .<sup>47, 51</sup> It suggests that every electron pair with relative distance *r* can be represented by a fictitious point, of which the density is given by  $P_a(\bar{r})$ .<sup>51</sup>

To replace the integration expression with the Patterson function yields,

$$I(\bar{Q}) = f_e^2 \int_{v} P_a(\bar{r}) e^{i\bar{Q}\bar{r}} d\bar{r}.$$
(57)

If the system has spherical symmetry, the same assumption that we made to derive Equations 33 and 43, we can then obtain,

$$I(Q) = 4\pi f_e^2 \int P_a(r) r^2 \frac{\sin(Qr)}{Qr} dr.$$
 (58)

# 2.1.4.3 Fourier Transform

Fourier transform (FT) was invented as a method to transform signals between time domain and frequency domain. It has now become essentially important in X-ray crystallography, where the same operation also functions between the real-space (r-space) and Q-space lattice. The detailed derivation<sup>43</sup> of the FT operations is not the main focus of the study, therefore only its application will be discussed here. Based on the literature<sup>43</sup>, the FT pairs have the following relations,

FT: 
$$F(s) = \int_{v} \rho(r) e^{2\pi i s r} dr$$
(59)

inverse FT: 
$$\rho(r) = \int_{v^*} F(s) e^{-2\pi i s r} ds.$$
(60)

According to these expressions, we can conclude from our previous derivation of the scattering relations that the atomic scattering factor  $f_a(\bar{Q})$  and the atomic electron density  $\rho_a(\bar{r})$  (Equation 32), the structure factor  $F(\bar{Q})$  and the electron density of a unit cell  $\rho(\bar{r})$  (Equation 39), and the scattering intensity  $I(\bar{Q})$  and the Patterson function  $P_a(\bar{r})$  are all FT pairs.

# 2.1.5 Small-angle X-ray Scattering (SAXS)

SAXS is a scattering technique which investigates the scattering event at low angles, where the scattering behavior is completely coherent because the Compton scattering (Section 2.1.1.1) can be neglected due to the low-angle nature of the technique. SAXS probes largescale structures with a length scale range that matches the size of many interesting and complex features in materials. In this thesis work, it is employed to extract the size and shape of the TiO<sub>2</sub>-B nanoparticles (Chapter 4) for structure model construction, in order to assist in the computation of the diffraction and PDF data.

#### **2.1.5.1 Prerequisites to the Equation Derivation**

Prior to the discussion of small-angle scattering, there are two assumptions that need to be made which will greatly simplify the understanding: i) isotropic system, resulting in scalarised vector equations, which play the same role as the basic assumption of spherical symmetry to yield the Equation 58; ii) no long-range order exists in the studied subjects. Therefore, the corresponding electron densities  $\rho(r)$  at large distance should be *r*-independent and can be replaced by the mean value  $\bar{\rho}$ .<sup>51</sup> So it is convenient to use the term,  $\Delta \rho(r)$ , which describes the electron density fluctuation, to replace the density  $\rho(r)$  itself, and the relation is given by  $\Delta \rho(r) = \rho(r) - \bar{\rho}$ . We can define a correlation function  $\gamma(r)$ , which has the following relation,

$$\Delta \,\tilde{\rho}^2(r) = V \gamma(r),\tag{61}$$

where V is the volume and  $\Delta \tilde{\rho}^2(\bar{r})$  stands for the self-correlation function (same as Equation 56), we can then derive the following relation from the Patterson function (Equation 58),

$$I(Q) = 4\pi f_e^2 \int V\gamma(r)r^2 \frac{\sin(Qr)}{Qr} dr$$
  
=  $V f_e^2 \int 4\pi r^2 \gamma(r) \frac{\sin(Qr)}{Qr} dr.$  (62)

Particularly, when Q=0,  $\lim_{Qr\to 0} (\sin(Qr)/Qr) = 1$ . Thereby all secondary waves are in phase:<sup>51</sup>

$$I(0) = V f_e^2 \int 4\pi r^2 dr \cdot \gamma(r).$$
(63)

#### 2.1.5.2 Shape Function

In practice,  $\rho(r)$  can be considered as the electron density of the finite sample while  $\bar{\rho}$  refers to the average density of the background, *i.e.*, solvent or air. Thus the  $\Delta \rho(r)$  in Equation 61 can be considered as constant, which is simply the electron density difference between the finite sample and the background.

Therefore, we can separate a very important term  $\gamma_0(r)$  from  $\gamma(r)$ , and obtain

$$\gamma(r) = \Delta \rho^2 \cdot \gamma_0(r) \; ; \; \gamma_0(0) = 1 ; \; \gamma_0(r \ge D) = 0, \tag{64}$$

where *D* corresponds to the dimension of the particle (for a sphere, D = 2R).  $\gamma_0(r)$  was first introduced by Porod and is called the characteristic function<sup>51</sup>. Apart from that,  $\gamma_0(r)$  has various other names depending on the application, such as shape function<sup>52</sup>/factor<sup>53</sup>, and nanoparticle form factor<sup>54</sup>, etc.. For clarity and consistency, the name "shape function" will be chosen hereafter because it gives the description of particle shape which is strongly coupled with the PDF (section 2.1.7) analysis on nanoparticles (chapter 4).

The shape function  $\gamma_0(r)$  can be defined as,

$$\gamma_0(r) = \frac{\tilde{V}(r)}{V(0)} = \frac{\tilde{V}(r)}{V},\tag{65}$$

where V(r) is the volume correlation function. Its physical meaning is the probability of finding a point within the V at a distance r from a given point.



Figure 2.6 A representation of the correlation function V(r)

Replacing  $\gamma(r)$  in the expression of I(0) (Equation 63) with  $\Delta \rho^2 \cdot \gamma_0(r)$ , we can expect I(0) to be equal to the square of the total number of electrons in the volume V: <sup>51</sup>

$$I(0) = V f_e^2 \int 4\pi r^2 dr \cdot \Delta \rho^2 \gamma_0(r)$$
  
=  $f_e^2 V \Delta \rho^2 \int 4\pi r^2 \gamma_0(r) dr$   
=  $f_e^2 V^2 \Delta \rho^2$ . (66)

If we substitute  $\gamma(r)$  in Equation 62 with  $\Delta \rho^2 \cdot \gamma_0(r)$ , and we can derive:

$$I(Q) = 4\pi f_e^2 \int_0^D \Delta \rho^2 V \gamma_0(r) r^2 \frac{\sin(Qr)}{Qr} dr$$
  
=  $\Delta \rho^2 V f_e^2 \int_0^D 4\pi r^2 \gamma_0(r) \frac{\sin(Qr)}{Qr} dr.$  (67)

The characteristic function  $\gamma_0(r)$  gives the probability of finding a pair of points in the particle with a distance *r* in an arbitrary direction. Hence it only depends on the geometry of the particle, and will be called as shape function hereafter. For some simple shapes, such as spheres, ellipsoids, cylinders and disks, etc, the shape functions can be achieved by geometry calculation.<sup>53, 55-56</sup>



Figure 2.7 Diagram of the (a) prolate and (b) oblate ellipsoids with major and minor radius labelled, where for prolate:  $r_{\text{major}} = av$ ,  $r_{\text{minor}} = a$ , while for oblate  $r_{\text{major}} = a$ ,  $r_{\text{minor}} = av$ .

The shape functions for spheres and ellipsoids (prolate and oblate) are shown as follows:

$$\begin{split} \gamma_{0}(r)_{sphere} &= \left(1 - \frac{r}{2a}\right)^{2} \left(1 + \frac{r}{4a}\right), \qquad (0 \le r \le 2a) \end{split} \tag{68} \\ \gamma_{0}(r)_{prolate} &= \begin{cases} 1 - \frac{3r}{8av} \left(1 - \frac{r^{2}}{16a^{2}} \frac{2}{v^{2}}\right) - \frac{3r}{8a} \left(1 - \frac{r^{2}}{16a^{2}}\right) \frac{v}{\sqrt{v^{2} - 1}} \tan^{-1} \sqrt{v^{2} - 1}, (0 \le r \le 2a) \\ 1 - \frac{3r}{8av} \left(1 - \frac{r^{2}}{16a^{2}} \frac{2}{v^{2}}\right) - \frac{3}{8} \left(1 + \frac{r^{2}}{8a^{2}}\right) \sqrt{1 - \frac{4a^{2}}{r^{2}}} \frac{v}{\sqrt{v^{2} - 1}} - \frac{3r}{8a} \left(1 - \frac{r^{2}}{16a^{2}}\right) \frac{v}{\sqrt{v^{2} - 1}} \\ \left(\tan^{-1} \sqrt{v^{2} - 1} - \tan^{-1} \sqrt{\frac{r^{2}}{4a^{2}}} - 1\right), (2a < r \le 2av) \end{cases} \end{aligned}$$

$$\begin{aligned} \gamma_{0}(r)_{oblate} &= \begin{cases} 1 - \frac{3r}{8av} \left(1 - \frac{r^{2}}{16a^{2}} \frac{2}{v^{2}}\right) - \frac{3r}{8a} \left(1 - \frac{r^{2}}{16a^{2}}\right) \frac{v}{\sqrt{1 - v^{2}}} \tan^{-1} \sqrt{1 - v^{2}}, (0 \le r \le 2av) \\ \frac{v}{\sqrt{1 - v^{2}}} \left[\frac{3a}{4v} \left(1 + \frac{r^{2}}{8a^{2}}\right) \sqrt{1 - \frac{4a^{2}}{r^{2}}} - \frac{3r}{8a} \left(1 - \frac{r^{2}}{16a^{2}}\right) \tan^{-1} \sqrt{1 - \frac{r^{2}}{4a^{2}}} \right], (2av \le r \le 2a) \end{cases} \end{aligned}$$

$$(69)$$

where v is the aspect ratio of the ellipsoids; a in  $\gamma_0(r)_{sphere}$  corresponds to the radius of the sphere; for a prolate shape (Figure 2.7a), a is the length of the minor radius  $(r_{minor})$  and v > 1, while in the case of an oblate (Figure 2.7b) model, a corresponds to the major radius  $(r_{major})$  and v < 1. The plotted shape functions for sphere, prolate and oblate ellipsoids are shown in Figure 2.8. Given that i) the ratios between the  $r_{major}$  and  $r_{minor}$  for the prolate (1.7) and oblate models (1.8) are close to each other; ii) these two ellipsoids have the same volume as the sphere with a radius of 15 Å, the profiles of the shape functions for these two ellipsoids are highly similar.

In practice, when the particle shapes cannot be defined using simple models, an accurate  $\gamma_0(r)$  can be obtained by the inverse FT (Section 2.1.4.3) of Equation 67:<sup>51</sup>



$$\Delta \rho^2 V f_e^2 \cdot \gamma_0(r) = \frac{1}{2\pi^2} \int_0^\infty Q^2 \cdot I(Q) \frac{\sin(Qr)}{Qr} dQ \,. \tag{71}$$

Figure 2.8 Shape functions for sphere, prolate and oblate ellipsoids. The ellipsoid models have the same volume as the sphere. The dimension of each model is listed in the legend.

#### 2.1.5.3 Data Analysis

In practice, it is very common that the particles are not monodisperse and/or not in a dilute system. Therefore, size distribution  $f_d(r)$  and/or interference  $S_i(Q)$  among particles need to be taken into account, which leads to a modification of intensity I(Q) based on Equation 50:

$$I(Q) = \left| \int F(Q) f_d(R) S_i(Q) dR \right|^2.$$
(72)

The structure functions for particles with simple shapes, *i.e.*, sphere and ellipsoid, and the equations accounting for distribution and interference are all included in the *Modeling II* tool of the Irena package<sup>57</sup>, which will be used in the SAXS data analyses.

## Structure Factor:

The derivation of F(Q) for a spherical particle (Equation 45) is shown section 2.1.3.2. For ellipsoids, the structure factor was derived on the basis of spherical geometry<sup>49</sup>, and is given by<sup>58</sup>

$$F(Q) = 3\rho_{0e}Vf_e \frac{\sin(QR) - QR\cos(QR)}{(QR)^3};$$

$$QR = \int_0^{\frac{\pi}{2}} Qa\sqrt{\cos^2\theta + v^2\sin^2\theta}\cos\theta \,d\theta$$

$$= \int_0^{\frac{\pi}{2}} Qa\sqrt{\cos^2\theta + \sin^2\theta + (v^2 - 1)\sin^2\theta} \,d\sin\theta$$

$$= \int_0^1 Qa\sqrt{1 + (v^2 - 1)x^2} \,dx,$$
(73)

where *a* is the major radius and *v* is the aspect ratio (v > 1 for prolate; v < 1 for oblate) of the ellipsoid (see Figure 2.7).

# Size Distribution:

The Schultz-Zimm size distribution<sup>59</sup> has been found to be adequate to represent many polydisperse systems<sup>60-63</sup> and therefore will be employed in the relevant analysis.

The distribution can be expressed as,

$$f_d(r) = \left(\frac{z+1}{\bar{r}}\right)^{z+1} \bar{r}^z \, e^{-(\frac{z+1}{\bar{r}} \cdot r)} / \Gamma(z+1) \,, \tag{74}$$

where  $\bar{r}$  is the mean radius of the particles, and z is the distribution width. The gamma function  $\Gamma(z+1)$  is given by  $\int e^{-t} t^{z-1} dt$ . In the Schultz-Zimm distribution, the maximum is at  $r_{max} = z\bar{r}/(z+1)$ , and the root mean square deviation from the mean is at  $\sigma = \bar{r}/\sqrt{z+1}$ .

# Interference:

The interference structure factor incorporated in the *Modeling II* tool is developed to approximate the inter-particle interference between hard spheres (meaning particles are impenetrable and cannot overlap in space).<sup>64</sup> Given that real particles are generally close to hard spheres, this structure factor can be employed for most practical purposes. It is given by<sup>57</sup>

$$S_i(Q) = \frac{1}{1 + 3\kappa \frac{\sin(Q\xi) - Q\xi\cos(Q\xi)}{(Q\xi)^3}},$$
(75)

where  $\kappa$  is the packing factor, and  $\zeta$  correspond to the correlation distance between particles.

# 2.1.6 X-ray Diffraction (XRD)

XRD is a phase and structural characterization technique founded on the constructive interference of the scattered X-ray, which is also called the Bragg diffraction. In this thesis work, it is employed for phase identification, particle size evaluation (chapter 5) and structure verification by comparing the computational and experimental patterns (chapter 4).

# 2.1.6.1 Bragg's Law



Figure 2.9 Diagram of the Bragg diffraction. Incident and scattered beams are denoted using blue and red arrows respectively; d corresponds to the interplanar spacing, and  $\theta$  is the scattering angle.

As illustrated in Figure 2.9, we assume incident waves with wavelength  $\lambda$  are scattered by two atoms O<sub>1</sub> and O<sub>2</sub> at the lattice planes  $p_1$  and  $p_2$  from the same family with indices *h*, *k*, *l*. The scattering angle is  $\theta$  and the spacing between the two planes is *d*. Therefore the difference in the propagation paths between the two waves is CO<sub>1</sub>+O<sub>1</sub>G, which equals 2*d* sin  $\theta$ . If only the coherent (Thomson) scattering (Section 2.1.1.2) is taken into account, Bragg showed that the scattered waves reach the maximum positive interference when the following relation is satisfied,<sup>44</sup>

$$2d\sin\theta = n\lambda\,,\tag{76}$$

where n is integer. In practice, the waves scattered by a crystal which consists of many planes interfere destructively if the above equation is not verified. Angles which verify the equation are called Bragg angles. In the study of scattering behavior on the basis of the plane family, ncan be simply considered as 1.

If we link the Bragg Equation with the momentum transfer Q (Equation 27) derived in section 2.1.2.1, we can obtain the direct relation between Q and the spacing d,

$$Q = \frac{4\pi \sin \theta}{\lambda} = \frac{4\pi \sin \theta}{2d \sin \theta} = \frac{2\pi}{d}.$$
 (77)

#### 2.1.6.2 Structure Factor in Terms of Indices

To derive the structure function  $F(\overline{Q})$  of the scattered waves which fulfill the Bragg's law, it is necessary to define the position of the scatterers first. In practice, people find it convenient to define atomic positions in a unit cell with respect to the origin via fractional coordinates.<sup>43</sup> If the unit cell dimension is denoted as *a*, *b* and *c*, their corresponding vectors  $\overline{a}$ ,  $\overline{b}$  and  $\overline{c}$  can be used to define a real space lattice. The position vector for an atom then becomes

$$\bar{r} = x\bar{a} + y\bar{b} + z\bar{c}.\tag{78}$$

In accordance with the  $\overline{a}$ ,  $\overline{b}$  and  $\overline{c}$  in real space, a new set of vectors  $\overline{a}^*$ ,  $\overline{b}^*$  and  $\overline{c}^*$  can be defined which have the following relations to the original vectors:

$$a \cdot a^* = 1, \qquad a \cdot b^* = a \cdot c^* = 0$$
  
 $b \cdot b^* = 1, \qquad b \cdot a^* = b \cdot c^* = 0$   
 $c \cdot c^* = 1, \qquad c \cdot a^* = c \cdot b^* = 0.$ 
(79)

This set of vectors defines the reciprocal lattice, which is also called as the Q space in X-ray crystallography. The scattering vector  $\overline{s}$  via the relation  $\overline{Q} = 2\pi \overline{s}$  (section 2.1.2.1) can then be expressed using the reciprocal lattice,

$$\bar{s} = h\overline{a^*} + k\overline{b^*} + l\overline{c^*}.$$
(80)

Upon obtaining the terms which describe the atomic position and the scattering vector, we can re-write the structure factor  $F(\bar{Q})$  in Equation 42 as

$$F(\bar{Q})_{hkl} = \sum_{j}^{N} f_{aj} e^{2\pi i \left(x_j \bar{a} + y_j \bar{b} + z_j \bar{c}\right) \cdot (h \overline{a^*} + k \overline{b^*} + l \overline{c^*})}.$$
(81)

Combining the relations in Equation 79, the expansion of the terms in brackets gives

$$F(\bar{Q})_{hkl} = \sum_{j}^{N} f_{aj} e^{2\pi i (hx_j + ky_j + lz_j)}.$$
(82)

#### 2.1.6.3 Scattering Intensity in Terms of Indices

Upon obtaining the structure factor in the form of indices, the intensity of the scattered waves given by Equation 50 can be computed. According to the assumption of a centrosymmetric distribution of the scatters (Equation 52), the imaginary part of the exponential in Equation 82

cancels each other out, with only the cosine function left. It finally yields an intensity function in terms of indices of reflections,

$$I(\bar{Q}) = \sum_{i}^{N} \sum_{j}^{N} f_{ai} f_{aj} \cos 2\pi \{h(x_i - x_j) + k(y_i - y_j) + l(z_i - z_j)\}.$$
 (83)

This equation holds whether or not there is a symmetry centre in the structure (details can be found in Friedel's  $law^{43-44}$ ).

We know from section 2.1.6.1, when the scattered waves at different Q meet the Bragg condition, they interfere constructively which leads to a maximum intensity. Therefore, a plot of I(Q) vs. Q yields peaks at specific Q values, corresponding to the Bragg reflections. The peak positions in terms of the Q values, according to the Bragg's law (Equation 77), are determined by the *d*-spacings of specific lattice planes in a crystal structure; the intensities, on the other hand, are dictated by the scattering factors (powers),  $f_a$ , of atom types, and their positions. Therefore X-ray diffraction (XRD) yields patterns explicitly depending on crystal structures, and is widely used to identify phases and to extract structural information.

#### 2.1.6.4 Data Simulation

To simulate XRPD patterns, a complete integration using Equation 83 over the whole reciprocal space (the detail of the integration algorithm is beyond the scope of this thesis, but can be found elsewhere<sup>44, 52</sup>) is usually the option for large particles that can be modeled as a periodic array of repeated unit cells. The atoms in these cells are related by symmetry operations, consequently resulting in a satisfactory computation speed. Therefore, this approach was employed to calculate XRPD patterns for large crystals in this thesis.

When the sizes of particles are very small, *i.e.*, nanoparticles, the crystal structure has a much lower periodicity and a smaller number of scatterers relative to large crystals. As a result, particles with finite sizes can no longer be modeled in the same manner as large crystals. In this thesis (see Chapter 4), the nanoparticle is presented as an ensemble of atoms, each residing in a unique position with no correlations between each other by symmetry operations. In that case, the Debye equation (Section 2.1.4.1), given by the summation of the contributions from each atom pair, was employed to calculate the XRPD pattern. It has proved to be faster than the complete integration in the simulation of diffraction data for nanoparticles. Additionally, to approximate the time average of the atomic positions in the structure due to thermal motions, the temperature factor (Equation 48 in Section 2.1.2.2) in terms of the thermal coefficient *B* was incorporated in the simulation<sup>65</sup>. The coefficient *B* was

converted from U via relation 49, while U for different atom species was obtained via the structure refinement of the PDF data<sup>66</sup>.

# 2.1.6.5 Scherrer Formula

If we compare the XRD patterns from two samples with one having a larger grain size than the other, assuming both samples have the same crystal structure and a uniform size distribution, the Bragg reflections for the smaller particles show a shorter and broader peak profile. Such a broadening effect due to the small size is attributed to a low degree of periodicity. As indicated by the intensity Equation 83, a higher periodicity from a larger crystallite causes more scattered waves to interfere in phase, reinforcing the diffraction, which results in a strong and narrow peak.

Paul Scherrer discovered that the width of the Bragg peak is able to quantitatively reflect the particle size, via the Scherrer formula<sup>67</sup>:

$$D_{\nu} = \frac{k\lambda}{\beta\cos\theta},\tag{84}$$

where  $D_{\nu}$  is the volume-weighted grain diameter<sup>68</sup>; *k* is the Scherrer constant, which varies around 1 depending on particle shape;  $\beta$  can be either the full width at half maximum (FWHM) or integral breadth (IB) in radians  $2\theta$ . IB is recommended for a more accurate size analysis,<sup>69</sup> which is the ratio between the peak area and the peak height. Note that evaluating and excluding the peak broadening from other contributions, such as instrumental and strain effect, is a prerequisite for size analysis. This important equation was employed to evaluate the particle size of the CuF<sub>2</sub> particles after ball-milling, which will be discussed in Chapter 5.

# 2.1.7 Pair Distribution Function (PDF)

PDF is a method derived from the scattering theory to investigate structures of materials having short-range order. Years ago, it was primarily applied to the study of the atomic structures in glasses and liquids which do not have structural periodicity.<sup>70</sup> This technique has recently shown a growing significance in the crystallography community due to the rising interest in nanomaterials. In addition, it is also a powerful technique in characterizing defects and disorders in bulk crystals where the local structure deviates from the average structure obtained via diffraction method.

Under the name of the pair distribution function, different researchers provided those functions which are essentially the same or similar with different names, leading to many confusions.<sup>71</sup> The nomenclature adopted in this thesis is mainly from the book by Egami and Billinge<sup>70</sup> with some slight modifications in order to keep the notations consistent with those as-defined terms in previous sections.

### 2.1.7.1 Normalized Structure Factor

Because the subject studied in PDF is atom-based correlation, therefore the sample structure factor  $F(\bar{Q})$  in Equation 39 can be re-defined per atom<sup>72</sup> as

$$F(\bar{Q}) = \langle f_a \rangle \int_{\nu} \rho_t(\bar{r}) e^{i\bar{Q}\bar{r}} d\bar{r} , \qquad (85)$$

where  $\langle f_a \rangle$  is the sample averaged atomic scattering factor, which is calculated by a compositional average of the atomic scattering factors over all atom types,

$$\langle f \rangle = \frac{1}{N} \sum_{\alpha} f_{\alpha} = \sum_{\alpha} c_{\alpha} f_{\alpha} , \qquad (86)$$

where  $\alpha$  denotes different atom types, and c is the concentration of the corresponding species with a relation to the total number of atoms, N, as  $c_{\alpha} = N_{\alpha}/N$ ;  $\rho_t(\bar{r})$  is the sample atomic density. Note that the atomic scattering factor  $f_a(\bar{Q})$  is a function of  $\bar{Q}$  (section 2.1.2.2), however the Q-dependence can be omitted to simplify the notation<sup>72</sup>, and the subscript a in  $f_a$ will be dropped for the same reason hereafter. It is necessary to define two other terms arising from the  $\langle f_a \rangle$ , which will be important in the intensity normalization to derive the PDF, <sup>70, 72</sup>

$$\langle f \rangle^2 = \left(\sum_{\alpha} c_{\alpha} f_{\alpha}\right)^2;$$
(87)

$$\langle f^2 \rangle = \sum_{\alpha} c_{\alpha} (f_{\alpha})^2.$$
(88)

If we consider a homogeneous atomic density on a microscopic level, the *r*-dependence of the  $\rho_t(\bar{r})$  can also be discarded. Hence  $\rho_t(\bar{r})$  can be replaced by the average number density  $\rho_0$ ,<sup>72</sup> and  $N_a$  will be simplified as *N* hereafter:

$$\rho_0 = \frac{N_a}{V} = \frac{N}{V},\tag{89}$$

and the normalized sample structure factor can be simplified as,

$$F(\bar{Q}) = \rho_0 \langle f_a \rangle \int_{\nu} e^{i\bar{Q}\bar{r}} d\bar{r}.$$
(90)

According to the re-defined structure factor, the I(Q) (Equation 67) derived in SAXS (section 0) can be re-written as

$$I(Q) = \Delta \rho_t^2 V \langle f \rangle^2 \int_0^D 4\pi r^2 \gamma_0(r) \frac{\sin(Qr)}{Qr} dr, \qquad (91)$$

where,  $\Delta \rho_t$  denotes the difference of the atomic density between the sample and the environment. Assuming an infinite solid and a vacuum (or air) environment with zero density, the  $\Delta \rho_t$  can be further substituted with the average number density of the solid  $\rho_0$ , and the upper limit of the integral is replaced with infinity. Finally we obtain

$$I(Q) = \rho_0^2 \langle f \rangle^2 V \int_0^\infty 4\pi r^2 \gamma_0(r) \frac{\sin(Qr)}{Qr} dr.$$
(92)

#### 2.1.7.2 Normalized Scattering Intensity

To derive the PDF, it is essential to first define  $S(\bar{Q})$ , the normalized scattering intensity<sup>52</sup>, which describes the discrete scattering intensity. It is also named as the total scattering structure function/factor elsewhere<sup>70</sup>, however, it is not an amplitude function like  $F(\bar{Q})$ . Therefore, the name of "normalized scattering intensity" is adopted to avoid confusion. It can be directly deduced from the Debye Equation (section 2.1.4.1) with self-scattering (i = j) part  $\sum_{i=j}^{N_a} f_{aj}^2 = N\langle f^2 \rangle$  removed. Note that in practice, scattering from microscopically isotropic crystallite samples is considered isotropic too. Therefore only the magnitude of  $\bar{Q}$  needs to be taken into account<sup>70</sup>. Then the Debye equation (Equation 53) becomes:

$$I(Q) = N\langle f^2 \rangle + \sum_{i}^{N} \sum_{j,i\neq j}^{N} f_i f_j \frac{\sin(Qr_{ij})}{Qr_{ij}};$$

$$\frac{I(Q)}{N} = \langle f^2 \rangle + \frac{1}{N} \sum_{i}^{N} \sum_{j,i\neq j}^{N} f_i f_j \frac{\sin(Qr_{ij})}{Qr_{ij}},$$
(93)

and S(Q) is obtained after the normalization by  $\langle f \rangle^2$ ,<sup>54, 72</sup>

$$S(Q) - 1 = \frac{I(Q)}{N\langle f \rangle^2} - \frac{\langle f^2 \rangle}{\langle f \rangle^2} = \frac{1}{N\langle f \rangle^2} \sum_{i}^{N} \sum_{j,i \neq j}^{N} f_i f_j \frac{\sin(Qr_{ij})}{Qr_{ij}}.$$
(94)

# 2.1.7.3 Derivation of the PDF in Theory

Upon obtaining the S(Q) - 1, the PDF  $G^*(r)$  in theory can be computed from the FT of the  $Q(S(Q) - 1)^{72}$ . Note that the asterisk superscript of G(r) indicates that the  $G^*(r)$  evaluated via the FT in Equation 95 deviates from the G(r) attained experimentally, which will be discussed in detail in Section 2.1.7.4.

$$\begin{aligned} G^{*}(r) &= \frac{2}{\pi} \int_{0}^{\infty} Q(S(Q) - 1) \sin(Qr) dQ \\ &= \frac{2}{\pi} \int_{0}^{\infty} \left[ \frac{1}{N\langle f \rangle^{2}} \sum_{i}^{N} \sum_{j,i\neq j}^{N} f_{i} f_{j} \frac{\sin(Qr_{ij})}{r_{ij}} \right] \sin(Qr) dQ \\ &= \frac{2}{N\langle f \rangle^{2} \pi} \int_{0}^{\infty} \sum_{i}^{N} \sum_{j,i\neq j}^{N} \frac{f_{i} f_{j}}{r_{ij}} \sin(Qr_{ij}) \sin(Qr) dQ \\ &= \frac{1}{N\langle f \rangle^{2} \pi} \int_{0}^{\infty} \sum_{i}^{N} \sum_{j,i\neq j}^{N} \frac{f_{i} f_{j}}{r_{ij}} \{ \cos[Q(r - r_{ij})] - \cos[Q(r + r_{ij})] \} dQ \end{aligned}$$
(95)  
$$&= \frac{1}{N\langle f \rangle^{2}} \cdot \frac{1}{2\pi} \int_{-\infty}^{+\infty} \sum_{i}^{N} \sum_{j,i\neq j}^{N} \frac{f_{i} f_{j}}{r_{ij}} \{ \cos[Q(r - r_{ij})] - \cos[Q(r + r_{ij})] \} dQ \\ &= \frac{1}{N\langle f \rangle^{2}} \cdot \frac{1}{2\pi} \int_{-\infty}^{+\infty} \sum_{i}^{N} \sum_{j,i\neq j}^{N} \frac{f_{i} f_{j}}{r_{ij}} \{ e^{iQ(r - r_{ij})} - e^{iQ(r + r_{ij})} \} dQ. \end{aligned}$$

Before further deduction, it is necessary to introduce the Dirac delta function  $\delta(r - r_i)^{44}$ , which is a mathematical expression of a series of atoms placed at positions  $r_i$  with respect to the position of origin at r. It has a particularly useful relation<sup>44</sup> which is essential in the derivation of the PDF,

$$\delta(r - r_i) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{iQ(r - r_i)} dQ.$$
 (96)

To replace the exponential parts in Equation 95 with Dirac delta functions gives

$$G^*(r) = \frac{1}{rN\langle f \rangle^2} \sum_{i}^{N} \sum_{j,i\neq j}^{N} f_i f_j \left\{ \delta(r - r_{ij}) - \delta(r + r_{ij}) \right\}$$
(97)

Considering only the positive *r*-values have physical meaning in our study,  $\delta(r + r_{ij})$  can be ignored,<sup>72</sup>

$$G^*(r) = \frac{1}{rN\langle f \rangle^2} \sum_{i}^{N} \sum_{j,i\neq j}^{N} f_i f_j \,\delta\big(r - r_{ij}\big). \tag{98}$$

If we compute the integral of  $G^*(r)r$  between two limits, *a* and *b*, to describe the number of atom pairs per atom within the separation between *a* and *b*, which is denoted as  $N_{ab}$ , we get

$$\int_{a}^{b} G^{*}(r) r dr = \int_{a}^{b} \frac{r}{r N \langle f \rangle^{2}} \sum_{i}^{N} \sum_{j, i \neq j}^{N} f_{i} f_{j} \,\delta(r - r_{ij}) \,dr$$

$$= \frac{1}{N \langle f \rangle^{2}} \sum_{i}^{N} \sum_{j, i \neq j}^{N} f_{i} f_{j} = \frac{1}{\langle f \rangle^{2}} \cdot \frac{1}{N} \sum_{i}^{N} f_{i} \sum_{j, i \neq j}^{N} f_{j}$$

$$\approx \frac{\langle f \rangle}{\langle f \rangle^{2}} \cdot \sum_{j}^{N} f_{j} \approx \frac{\langle f \rangle^{2}}{\langle f \rangle^{2}} N_{ab}$$

$$= N_{ab}.$$
(99)

Thus over a whole *r*-scale, we can derive,

$$\int G^*(r)rdr = N_p,\tag{100}$$

where  $N_p$  stands for number of atom pairs. If we define  $\rho_p(r)$  as the pair density (note that the subscript p is adopted to differentiate between the pair density and the electron density  $\rho(r)$  (section 2.1.3.1), although  $\rho(r)$  is more commonly used to define the pair density in literature<sup>70</sup>), and R(r) as the radial distribution function, we are able to derive following relations based on the definition of these two terms,

$$N_p = \int_{\mathcal{V}} \rho_p(r) d\bar{r} = \int R(r) dr.$$
(101)

Comparing Equation 100 and 101, we can correlate  $G^*(r)$ ,  $\rho_p(r)$ , and R(r) by

$$\int G^*(r)rdr = \int_{\mathcal{V}} \rho_p(r)d\bar{r} = \int R(r)dr.$$
(102)

On the basis of the volume integration in Equation 34, we know

$$\int_{v} \rho_{p}(r) d\bar{r} = \iiint r^{2} \rho_{p}(r) \sin \varphi \, d\varphi d\theta dr = \int_{v} 4\pi r^{2} \rho_{p}(r) d\bar{r} \,. \tag{103}$$

We can then finally obtain,

$$G^{*}(r) = \frac{R(r)}{r} = 4\pi r \rho_{p}(r).$$
(104)

# 2.1.7.4 Deduction of the PDF in Practice



Figure 2.10 Picture of the transmission geometry of the PDF experiment, taken at beamline 11-ID-B at the Advanced Photon Source (APS). L is the dimension of the 2-dimensional (2D) detector, while l corresponds to the diameter of the beamstop; d is the beamstop-to-detector distance, and D is the sample-to-detector distance;  $2\theta$  is the scattering angle.

The sine FT of Q(S(Q) - 1) in Equation 95 is given by the integral over the Q range  $(0,\infty)$ . However, the normalized intensity S(Q) in practice is measured over a finite range  $(Q_{\min}, Q_{\max})$ . Consequently, the G(r) is limited by the Q cutoff from the experiments. As illustrated in Figure 2.10, the  $2\theta_{\max}$ , which is limited by the size of the 2-dimensional (2D) detector and sample-to-detector distance, determines  $Q_{\max}$ :

$$Q_{max} = \frac{4\pi}{\lambda} \sin\left(\frac{1}{2} \tan^{-1}\frac{L}{2D}\right). \tag{105}$$

The  $Q_{\min}$  is, however, dictated by the size and position of the beamstop, and is given by

$$Q_{min} = \frac{4\pi}{\lambda} \sin\left(\frac{1}{2} \tan^{-1} \frac{l}{2(D-d)}\right).$$
 (106)

The termination of the PDF computation at  $Q_{\text{max}}$  has been well understood, and can be interpreted as applying a broadening function,  $\sin(Q\Delta r) / \Delta r^{73}$ . Therefore the following discussion only focuses on the impact of  $Q_{\text{min}}$ .

To change the limits of the Fourier integral according to the experimental limits,

$$\begin{aligned} G(r) &= \frac{2}{\pi} \int_{Q_{min}}^{Q_{max}} Q(S(Q) - 1) \sin(Qr) \, dQ \approx \frac{2}{\pi} \int_{Q_{min}}^{\infty} Q(S(Q) - 1) \sin(Qr) \, dQ \\ &= \frac{2}{\pi} \int_{0}^{\infty} Q(S(Q) - 1) \sin(Qr) \, dQ - \frac{2}{\pi} \int_{0}^{Q_{min}} Q(S(Q) - 1) \sin(Qr) \, dQ \\ &= G^*(r) - \frac{2}{\pi} \int_{0}^{Q_{min}} Q(S(Q) - 1) \sin(Qr) \, dQ \\ &= 4\pi r \rho_p(r) - G(r)^{SAXS}, \end{aligned}$$
(107)

where the limits of the Fourier integral (0,  $Q_{\min}$ ) implies that the deviation from the experimental G(r) to the theoretical  $G^*(r)$  arises from the small-angle scattering.

To elucidate the impact of SAXS on the PDF, it is necessary to evaluate the  $Q_{\min}$  cutoff on the Q(S(Q) - 1) before the sine FT. From the definition of S(Q) and also on the basis of the redefined I(Q) in Equation 92, we can derive

$$Q(S(Q) - 1) = Q\left(\frac{I(Q)}{N\langle f \rangle^2} - \frac{\langle f^2 \rangle}{\langle f \rangle^2}\right)$$

$$= Q\left(\frac{\rho_0^2 \langle f \rangle^2 V}{N\langle f \rangle^2} \int_0^\infty 4\pi r^2 \gamma_0(r) \frac{\sin(Qr)}{Qr} dr - \frac{\langle f^2 \rangle}{\langle f \rangle^2}\right)$$

$$= Q\left(\frac{\rho_0 \cdot (\rho_0 V) \cdot \langle f \rangle^2}{N\langle f \rangle^2} \int_0^\infty 4\pi r^2 \gamma_0(r) \frac{\sin(Qr)}{Qr} dr - \frac{\langle f^2 \rangle}{\langle f \rangle^2}\right)$$

$$= Q\left(\rho_0 \int_0^\infty 4\pi r^2 \gamma_0(r) \frac{\sin(Qr)}{Qr} dr - \frac{\langle f^2 \rangle}{\langle f \rangle^2}\right)$$

$$\approx Q \rho_0 \int_0^\infty 4\pi r^2 \gamma_0(r) \frac{\sin(Qr)}{Qr} dr$$

$$= \int_0^\infty 4\pi r \rho_0 \gamma_0(r) \sin(Qr) dr,$$
(108)

where term  $\langle f^2 \rangle / \langle f \rangle^2$  is very small compared to the first one, thus can be ignored. The final form of the Q(S(Q) - 1) is a sine integral, hence the inverse FT of this Equation gives rise to<sup>72</sup>

$$\frac{2}{\pi} \int_0^\infty Q(S(Q) - 1) \sin(Qr) \, dQ = 4\pi r \rho_0 \gamma_0(r).$$
(109)

The next step is the evaluation of the sine Fourier integral over the Q range  $(0, Q_{\min})$ . Note that the PDF is derived from the FT of term Q(S(Q) - 1), which only includes the discrete scattering intensity of the Debye Equation,  $\sum_{i}^{N} \sum_{j,i\neq j}^{N} f_i f_j [\sin(Qr_{ij})/Qr_{ij}]$  (Equation 94). It is therefore useful to assess the impact of the coupled term Qr on the normalized intensity first.

To help the discussion, let us consider two cases: i) a crystallite with a finite size (r = D), and ii) a large (infinite) crystal solid ( $r \gg D$ ) with a uniform number density  $\rho_0$ . When the *Q* is confined in the SAXS region at very small  $Q_{\min}$ , the value of the term Qr is mostly defined by  $Q_{\min}$  instead of the dimension of the measured subject, consequently leading to  $\sin(Qr_{ij})/Qr_{ij} \approx 1$  (see derivation of Equation 63) for both small crystallites and large solids. That means the normalized intensities  $S(Q)^{SAXS}$  for crystallites and solids should be the same. Thus we derive:

$$Q(S(Q)_{crystalite}^{SAXS} - 1) = Q(S(Q)_{solids}^{SAXS} - 1)$$
  

$$\Rightarrow G(r)_{crystalite}^{SAXS} = G(r)_{solids}^{SAXS}.$$
(110)

Note that the deduction of Equation 109 is based on the assumption of infinite solids with uniform density (Equation 92), therefore  $G(r)_{solids} = 4\pi r \rho_0 \gamma_0(r)$ . If we correlate it with the relation 110, we can get:

$$G(r)^{SAXS} = G(r)_{solids} = 4\pi r \rho_0 \gamma_0(r).$$
(111)

Finally the G(r) measured over the experimental Q range of  $(Q_{\min}, Q_{\max})$  can be expressed as:

$$G(r) = 4\pi r \rho_p(r) - 4\pi r \rho_0 \gamma_0(r).$$
(112)

Although the shape function  $\gamma_0(r)$  has a significant meaning for crystallites with finite sizes, however, it reaches unity for large crystals,  $\gamma_0(r) \cong 1$ . So the PDF for large crystals can be written as:

$$G(r) = 4\pi r \rho_p(r) - 4\pi r \rho_0, \qquad (113)$$

which is the most common expression usually seen in literature<sup>74</sup>.

# 2.1.7.5 Data Analysis

The PDF analyses in this thesis consist of two parts, i) simulation and ii) refinement.

# Simulation:



Figure 2.11 Example of  $G^*(r)$  (green) and G(r) (black solid) calculated using an oblate TiO<sub>2</sub>-B particle. The baseline correction function without (black dashes) and with (blue, orange and red) the shape factors  $\gamma_0(r)$  are shown below the y = 0 dotted line. The radius used in the sphere model (blue dash-dot) is 15.0 Å in radius; the prolate (orange dash) has a 21.5 Å major axis radius and 12.5 Å minor axis radius; the oblate (red solid) has a 18.4 Å major axis radius and 10.0 Å minor axis radius. The corresponding  $\gamma_0(r)$  for each shape is illustrated in Figure 2.8.

Simulation was performed on the nanoparticles with non-spherical shapes, *i.e.*, ellipsoids (see Chapter 4). The PDF is computed from the final form of the  $G_{calc}(r)$  from the G(r) derived from Equation 112,

$$G_{calc}(r) = kB(r)G(r) = kB(r)[G^{*}(r) - 4\pi r\rho_{0}\gamma_{0}(r)]$$
(114)  
= kB(r) [4\pi r\rho\_{p}(r) - 4\pi r\rho\_{0}\gamma\_{0}(r)],

where k is the scaling factor and B(r) is a damping function which accounts for the instrumental Q resolution, and is given by

$$B(r) = e^{-\frac{(rQ_{damp})^2}{2}}.$$
(115)

The variable  $Q_{damp}$  is instrument-dependent, which can be obtained by refining a standard reference sample, such as Ni powder. The part accounting for  $G(r)^{SAXS}$  can be considered as a baseline correction (see Figure 2.11).

Replacing  $G^*(r) = 4\pi r \rho_p(r)$  using Equation 98 leads to:

$$G_{calc}(r) = kB(r) \left( \frac{1}{rN} \sum_{i}^{N} \sum_{j,i\neq j}^{N} \frac{f_i f_j}{\langle f \rangle^2} \delta(r - r_{ij}) - 4\pi r \rho_0 \gamma_0(r) \right).$$
(116)

For prolate and oblate particles, the shape functions  $\gamma_0(r)_{prolate}$  and  $\gamma_0(r)_{oblate}$  are taken from Equation 69 and 70, respectively. The delta function  $\delta(r - r_{ij})$  (Equation 96) which represents the atomic positions can be replaced with a Gaussian distribution function<sup>52</sup>,  $T_{ij}(r)$ , to account for the thermal motions,

$$T_{ij}(r) = \frac{1}{\sqrt{2\pi}\sigma_{ij}(r)} e^{\left[\frac{-(r-r_{ij})^2}{2\sigma_{ij}^2(r)}\right]} \cdot \left(1 + \frac{r-r_{ij}}{r_{ij}}\right).$$
 (117)

Note that the first part of the function is simply a Gaussian, and it is multiplied by a modification function,  $1 + (r - r_{ij})/r_{ij}$ , to account for the anisotropic difference between the actual peak shape and the Gaussian approximation<sup>75</sup>. The Gaussian width,  $\sigma_{ij}(r)$ , shows an *r*-dependent relation:

$$\sigma_{ij}(r) = \sqrt{\sigma'_{ij}^2 - \frac{\delta}{r_{ij}^2} - \frac{\gamma}{r_{ij}} + \alpha^2 r_{ij}^2},$$
(118)

where  $\delta$  and  $\gamma$  model the low-temperature and high-temperature behaviours, respectively<sup>66</sup>;  $\alpha$  models the peak broadening due to the instrument<sup>52, 66</sup>.

To simplify the notation, the subscript in  $G_{calc}(r)$  will be dropped in later chapters. It must be born in mind that although the calculated PDFs are denoted as G(r), they are all computed as  $G_{calc}(r)$  using Equation 116.

An example of  $G^*(r)$  and G(r) is shown in Figure 2.11. The relation between the shape-dependent  $\gamma_0(r)$  and the baseline correction is also illustrated. Note that the two ellipsoid models and the sphere all have the same volume. The difference in the profile between the two ellipsoid models is very small, however, significant when the ellipsoids are

compared with the sphere (particularly at high *r*-regions). The comparisons indicate the sensitivity of PDF to the particle shape between sphere and ellipsoid.

# Refinement:

Structure refinement was performed using the PDFgui software<sup>76</sup> on large crystals, *i.e.*, LiVO<sub>2</sub> (Chapter 3), and (spherical) nanoparticles, *i.e.*, CuF<sub>2</sub> (Chapter 5). The refinement runs on a real-space Rietveld code, using a least-squares approach, to refine a theoretical PDF profile until it matches the measured profile.<sup>76</sup> The structure analysis is performed on a small repeating unit, *i.e.*, unit cell. For nanoparticles, the structure is modelled by assuming a spherical shape ( $\gamma_0(r)_{sphere}$ ) with a refinable radius. The weighted agreement factor of the refinement,  $R_w$  is given by<sup>77</sup>,

$$R_{w} = \sqrt{\frac{\sum_{i=1}^{N} w(r_{i}) \left[G_{exp}(r_{i}) - G_{calc}(r_{i})\right]^{2}}{\sum_{i=1}^{N} w(r_{i}) G_{exp}^{2}(r_{i})}},$$
(119)

where  $G_{exp}(r)$  and  $G_{calc}(r)$  are the observed experimental and calculated PDFs, respectively; *w* is the weighting factor.

# 2.2 X-ray Absorption

The topic in this section is about absorption, which is the other interaction apart from scattering between the X-ray photon and the sample.

# 2.2.1 X-ray Absorption Spectroscopy (XAS)

The prerequisite for the absorption to occur is that the X-ray photon needs to have a higher energy than the binding energy of the atoms, which gives rise to the photoelectric effect.<sup>78</sup> As illustrated in Figure 2.12a, during the absorption process, a photon is absorbed by the atom. The photon energy is taken to promote the electron,  $e_1$ , out of the core-shell (K) of the absorber element, into the continuum.



Figure 2.12 Diagram of (a) the X-ray absorption process and (b) the experiment geometry. Black circles in (a) denote the holes that are left after the electron excitation. Red and green arrows signify the fluorescence and Auger mechanisms, respectively.

Figure 2.12b gives a simple geometric relation between the incident  $(I_0)$  and the transmitted (I) X-rays. The intensities of these two photon beams before and after hitting sample obey the Beer's law,

$$I = I_0 e^{-\mu(E)x}$$
  

$$\Rightarrow \mu(E)x = -\ln\frac{I}{I_0},$$
(120)

where  $\mu$  is the absorption coefficient and *E* means the  $\mu$  is energy-dependent; *x* is the sample thickness. Based on this equation, the absorption of the X-ray radiation on a sample can be measured as a function of X-ray energy, and such technique is called the X-ray absorption spectroscopy (XAS). Due to the  $Z^4$ -dependence (*Z* is the atomic number) of the absorption coefficient, the  $\mu$  for various elements are highly different from each other. Therefore, XAS is an element-specific technique.
### 2.2.2 Decay Behaviors

Note that following the excitation of the core-level electron, the atom at the excited state will decay to reach the minimal energy state. The decay mechanism (Figure 2.12a) involves an electron,  $e_2$  or  $e_3$ , at higher energy levels (L or M) than the core-level (K), jumping back to fill the core hole in the inner shell and ejecting an X-ray photon ( $I_f$ ) with well-defined energy. Such decay mechanism is named as fluorescence. Depending on the level of the electron sites, the fluorescence X-ray is defined as  $K_a$  and  $K_\beta$  for L and M level respectively. In addition to fluorescence, the decay mechanism sometimes occurs via another path, called the Auger effect, which yields a photoelectron named an Auger electron. Because both the fluorescence line and the Auger emission are element specific, their intensities can also be monitored to evaluate the absorption coefficient. The relevant geometry for these measurements is normally conducted in reflection mode, which is illustrated in Figure 2.12b in contrast to the transmission mode for a common measurement of  $I_0$  and I. However, the decay mechanisms are beyond the scope of this thesis work. The following discussion will therefore focus on the absorption behavior only. Details regarding the fluorescence and Auger measurements can be referred to literature<sup>79-80</sup>.



### 2.2.3 X-ray Absorption Fine Structure (XAFS)

Figure 2.13 The compositions of XAFS. Black curve is the experimental XAS data of Cu metal; green dashed line is the 1st derivative of the corresponding XAS data;  $E_0$  marks the Cu K-edge position; Red and blue rectangular boxes denote the XANES and EXAFS region of the XAS data, respectively.

The information delivered by the X-ray absorption spectrum is sometimes named as X-ray absorption fine structure  $(XAFS)^{79}$ . Figure 2.13 shows the plot of the normalized absorption coefficient for Cu metal as a function of energy *E* in the range of 8950 – 9400 eV. The data contains two distinct features: i) a low energy line followed by a steep rise at a certain energy called edge (*E*<sub>0</sub>), which can be determined accurately by locating the first peak in the 1st derivative of the corresponding spectrum; ii) wiggles and oscillations above the edge position. The first feature, which covers the energy range about 50 eV around the edge position (*E*<sub>0</sub>), is called the X-ray absorption near edge structure (XANES); the other feature is the extended X-ray absorption fine structure (EXAFS).

The small feature at the pre-edge region ( $E < E_0$ ) is usually attributed to the electron transitions from the core level to the higher unfilled or half-filled orbitals, such as  $s \rightarrow p$ , or  $p \rightarrow d$ . The XANES (Section 2.2.4) region is ascribed to the transitions of core electrons to non-bound levels with very close energy, the probabilities of which are very high thus leading to a sharp raise of the absorption. The wiggles after the rising edge are attributed to the multiple scattering of the photoelectrons by the neighbouring atoms in the first or higher coordinating shells. In the EXAFS region, where the ejected photoelectrons have higher energy, the oscillation is associated with the single scattering of these ejected photoelectrons by the nearest neighbouring atoms.<sup>79</sup> Thus EXAFS is commonly used to determine the atomic pair distribution. Give that the atomic pair distribution can also be derived from the PDF (Section 2.1.7) technique, in the relevant XAS experiment, only the XANES region was studied in this thesis work. In the following section, the topic of the discussion will be only about XANES. Information regarding EXAFS can be found in literature<sup>79-82</sup>.

### 2.2.4 X-ray Absorption Near Edge Structure (XANES)

### 2.2.4.1 Data Normalization

The purpose of the normalization is to regularize the spectra with respect to the variations in the sample and the experiment setup so that the normalized data can be directly compared to each other regardless of the experiment details.<sup>83</sup> Figure 2.14a shows the un-normalized  $\mu(E)$ , in contrast to the normalized absorption spectrum in Figure 2.14b, the distinct difference between the two is the slopes of the pre-edge and post-edge lines.



Figure 2.14 XANES spectra for  $CuF_2$  (a) before and (b) after normalization. Pre- and postedge lines for normalization are highlighted with red and blue lines, respectively. The magnified pre-edge feature is shown in the inset (c).

The first step of normalization is to obtain the normalization constant,  $\Delta \mu_0(E)$ , by locating the  $E_0$  position, and fitting the pre-edge and post-edge lines (with simple polynomials).<sup>83</sup>  $\Delta \mu_0(E)$ , also known as the "edge step", can be evaluated by extrapolating these lines to  $E = E_0$  and subtracting the zero-crossing of the pre-edge line from that of the post-edge line. To get rid of the instrumental background, the pre-edge line can be subtracted from the  $\mu(E)$ , and therefore putting the pre-edge at zero.<sup>79</sup> The normalization of the  $\mu(E)$  from 0 to 1 is performed using the edge step normalization constant  $\Delta \mu_0(E)$ . The last procedure is to flatten the post-edge line, consequently leading to an oscillation around  $\mu(E) = 1$ . The removal of the shape difference in this post-edge region is believed to simplify further analyses<sup>83</sup>, such as the linear combination analysis (LCA), and principal component analysis (PCA), etc.

#### 2.2.4.2 Qualitative Analysis

### $Pre-edge(< E_{\theta}):$

As mentioned previously, the pre-edge feature corresponds to the electron transition from the core level to higher unfilled orbitals. In the case of 3d transition metals, it is usually ascribed to the  $1s \rightarrow 3d$  transition, sometimes with few percent of 4p mixing<sup>80</sup>. The exact nature of the transition and the relative intensity of the pre-edge peak (if there is one) highly depend on the coordination geometry of the target atom, and are determined by the selection rule and group theory. For the same target elements with the same oxidation state, the preedge peak for the tetrahedrally-coordinated atom has a higher intensity than the octahedrallycoordinated counterpart<sup>84</sup>, because  $1s \rightarrow 3d$  transition is dipole forbidden for centrosymmetric geometry (such as, octahedral, square planar, linear, etc.), leading to small intensities for octahedral environments (Figure 2.14c); while 3d + 4p mixing occurs in the tetrahedral geometry, giving rise to dipole-allowed  $1s \rightarrow 3d + 4p$  transitions, hence a higher intensity. Details about the understanding of the pre-edge feature can be found in literature<sup>80</sup>, <sup>84-85</sup>



Figure 2.15 (a) Normalized Cu K-edge XANES spectra of Cu metal and Cu reference compounds: Cu<sub>2</sub>O, Cu<sub>2</sub>S, CuCl, CuO, CuF<sub>2</sub>, CuCl<sub>2</sub>; (b) 1st derivatives of the normalized Cu K-edge XANES spectra shown in (a). The  $E_0$  positions of each reference are marked with dot lines.

### $E_0$ position:

The edge position  $E_0$  depends on the oxidation state of the target atoms. Figure 2.15 shows the XANES of a series of references for the Cu K-edge experiment, which contains Cu with different oxidation states, various bonding elements and coordination geometries. The relation between the oxidation state and the edge energy can be evaluated by comparing the  $E_0$  of the spectra between Cu, Cu(I)<sub>2</sub>O and Cu(II)O, where we can observe a higher oxidation state corresponds to a more positive  $E_0$ ; Comparing the  $E_0$  between Cu(II)O, Cu(II)Cl<sub>2</sub> and

Cu(II)F<sub>2</sub>, we can conclude that for the same atoms with the same oxidation state, a higher electronegativity of the neighbouring atom leads to a higher  $E_0$ ;

### Wiggles (> $E_0$ ) and the 1st Derivatives:

The wiggles beyond the rising edge are attributed to the multiple scattering of the photoelectrons by the neighbouring atoms in the first or higher coordinating shells. Therefore, these spectral regions conceal information about the local geometry of the target information. An earlier Cu K-edge XANES study on a series of compounds containing Cu with various coordination geometries revealed that the line shapes of the XANES spectra and the corresponding 1st derivatives have shown a great dependence on the local geometry of the Cu atoms, and those Cu in similar coordination environments gave rise to a similar profile of the XANES spectra and the 1st derivatives.<sup>86</sup> The result indicated that the line shapes of the XANES spectra and the corresponding 1st derivatives.<sup>86</sup> The result indicated that the line shapes of the XANES spectra and the corresponding 1st derivatives can be used as fingerprints to identify the local geometry of the target atoms.

Table 2.1 The Cu local environments in the standard samples for reference.

	Cu <sub>2</sub> O	$Cu_2S^{87}$	CuCl	CuO	CuCl <sub>2</sub>	CuF <sub>2</sub>
geometry	linear	triangular	tetrahedral	square planar	octahedral (JT)	octahedral (JT)
coordination	2	3	4	4	6	6

Table 2.1 lists the Cu coordination environments in the reference compounds whose spectra are shown in Figure 2.15. An approach based on the aforementioned fingerprinting theory, in combination with the PCA and target transformation (TT) analysis, was employed on the XANES data of these reference standards and the  $CuF_2$  battery, in order to predict and verify an unknown species present in the charge process. The detailed discussion can be referred to Section 5.3.3.

#### 2.2.4.3 Linear Combination Analysis (LCA)

The LCA is a mathematical method to fit the unknown spectra using a linear combination of standard spectra:

$$\mu(E) = \sum_{j}^{N} c_{j} \mu_{j}(E); 1 = \sum_{j}^{N} c_{j}, \qquad (121)$$

where  $c_j$  corresponds to the molar concentration of the corresponding component *j*. Therefore, LCA is a quantitative approach. In this thesis work, the LCA was performed on a series of

XANES data from an in situ XAS experiment on the  $CuF_2$  conversion reaction (Chapter 5), which is theoretically a 2-phase reaction. Thus the spectrum acquired at any state during the (dis)charge process is expected to consist of two end members,  $CuF_2$  and Cu. The LCA output can be used to track the concentration evolution of every component, which assists in the understanding of reaction kinetics and mechanism.

# 2.2.4.4 Principal Component Analysis (PCA)

The PCA is a mathematical approach to decompose a set of data into the minimum number of components that are needed to describe the variance in the data. The basic idea of performing PCA is to determine the minimum number of standard references to describe a series of XANES spectra. In this specific work, PCA was performed to evaluate the number of possible phases (end members) in the  $CuF_2$  charge reaction (Section 5.3.3).

The output of the PCA on a set of XANES spectra are a series of components, composed of principal and non-principal members. The non-principal components simply refer to noise, while the principal ones contain sufficient signal to reconstruct each experimental spectra mathematically via a linear combination.<sup>88</sup> The detailed algorithm can be found in reference<sup>89</sup>.

## 2.2.4.5 Target Transformation (TT)

The TT is a mathematical approach to determine whether a potential reference spectrum can be legitimately considered as an end-member standard for LCA. The basic procedure is to evaluate whether the potential reference can be reproduced by a linear combination of the principal components obtained from PCA. The purpose of employing this analytical method in this thesis work is to associate with the PCA result to determine the unknown phase in the  $CuF_2$  charge reaction (Section 5.3.3).

# 2.3 Other Techniques

# 2.3.1 Electrochemistry

Within the scope of this thesis work, three electrochemistry techniques were employed to study battery reactions.

# 2.3.1.1 Galvanostatic Cycling

Galvanostatic cycling is the most basic and important electrochemistry technique, which directly measures the instantaneous voltage response to a constant current applied to the battery. The resultant plot of the operating voltage as a function of current gives a voltage curve, which can be used to determine the cell capacity and reversibility, and to evaluate the effect of cycling rate and temperature. The rate of cycling, denoted as C/n, is computed based on the theoretical capacity,  $C_{th}$  (Equation 4), and mass of the active material in the battery (m).

$$C/n = \frac{m \cdot C_{th}}{n}.$$
(122)

The interpretation of C/n is the current magnitude that is needed to reach the theoretical capacity ( $C_{th}$ ) within the number of hours (n).

# 2.3.1.2 Cyclic Voltammetry (CV)

In contrast to the galvanostatic cycling, CV is a potentiostatic measurement, which measures the current response to a linear sweep of voltage. Within the applied voltage window, current peaks appear at the potentials where the redox reactions take place. Depending on the subjects being studied, both thermodynamic (such as reaction potential) and kinetic information (such as electron transfer) can be extracted from the resulting voltammogram<sup>90</sup>. The purpose of employing this technique in this thesis was to investigate the characteristics of the redox couples in the CuF<sub>2</sub> conversion reactions (Chapter 5) from the positions and magnitudes of the current peaks within the charge and discharge cycles.

# 2.3.1.3 Galvanostatic Intermittent Titration (GITT)

In practice, the operating potential of a battery is always lower in discharge, and higher in charge, as compared to the theoretical potential. The voltage difference between the operating and the theoretical potential is defined as overpotential, which is governed by many facts, such as  $Li^+$  concentration gradient in the electrolyte, and electronic resistance from the battery

components, etc. The overpotential is directly related to the voltage efficiency of the battery, which is among the selection criteria for commercial battery systems.

GITT is an analytical electrochemical method to evaluate the voltage efficiency, via the measurement of the overpotential upon electrochemistry cycles. The experiment is conducted under galvanostatic condition which consists of a series of current pulses, each followed by a relaxation process, in which no current applied to the battery. During the resting process, the potential of the battery gradually reaches the equilibrium, which ideally resembles the theoretical potential. Therefore, the voltage difference before and after the relaxation is considered as the overpotential. In addition, the equilibrium voltage curve, acquired from the GITT and very often drastically different from the operating voltage curve due to the overpotential, reflects the nature of the battery reaction according to the Gibbs phase rule<sup>91</sup>. To this end, GITT was employed in this thesis work to evaluate the overpotential and the mechanism of the  $CuF_2$  2-phase reaction, which will be discussed in detail in Chapter 5.

# 2.3.2 Solid State Nuclear Magnetic Resonance (NMR) Spectroscopy

Apart from PDF (Section 2.1.7), solid state NMR is another powerful technique in crystal structure determination at the atomic level. In contrast to the X-ray experiments which sometimes encounter radiation damage of the sample, NMR is a non-destructive and non-invasive technique. The measurement is isotopically specific and nearly all elements have spin-active nuclei that can be accessed, therefore NMR can be applied to the vast majority of samples. Most importantly, the sensitivity of NMR is sufficient to detect nuclei with large magnetogyric ratios at relatively low concentrations, and does not have a Z-dependence (Z, atomic number) like the X-ray technique (Equation 37: the atomic scattering factor  $f_a$  is a spherical average over the total number of electrons in the atom,  $Z \cdot f_e$ ) does. Hence NMR can be used to probe species containing light elements, such as Li and C.

The basic NMR experiment<sup>92</sup> is performed by i) allowing the magnetic nuclear spins to reach equilibrium in the presence of a large external magnetic field  $\overline{B}_0$ ; ii) applying a radiofrequency (RF) pulse to rotate the nuclear spin magnetism vector  $\overline{M}$ ; iii) detecting and amplifying the weak RF signal, which is called free-induction-decay (FID), generated by nonequilibrium spin magnetizations precessing (Figure 2.16b) about the magnetic field.

## 2.3.2.1 Magic Angle Spinning (MAS)



Figure 2.16 (a) Diagram of the magic angle spinning experiment.  $B_0$  refers to the magnitude of the external magnetic field, the direction of which is normally set along *z*-axis. The rectangular box denotes the sample container (rotor) in a solid state NMR experiment. The angle  $\theta = 54^{\circ}44'$  between the spinning axis of the rotor and direction of the external magnetic field is the magic angle. (b) Illustration of the precession of the bulk magnetization vector of the sample,  $\overline{M}$ . During the precession, the rotating magnetization vector induces a current in the coil that is wound around the *y*-axis. This current is then amplified and recorded as the NMR signal.

In contrast to the solution NMR, where fast molecular motion effectively removes all the anisotropic interactions present in a molecule therefore leading to sharp resonances with good

resolution, solid state NMR gives broad resonances due to the lack of the molecular motions. Therefore special methods need to be employed to enhance the spectral resolution and allow distinguishing the chemical shifts of nuclei in different chemical environment. To this end, the magic angle spinning (MAS) (Figure 2.16) is employed in the solid state NMR experiment to improve the resolution by suppressing the broadening due to the anisotropic interactions. All anisotropic interactions have an orientation dependence of the form  $(3\cos^2\theta-1)^{93}$ , where  $\theta$  is the angle between the sample container and the external magnetic field. At the magic angle,  $\theta = 54^{\circ}44^{\circ}$ , this term becomes  $3\cos^2\theta - 1 = 0$ , resulting in at least partial averaging of the anisotropic interactions. More details about the various interactions that are present in solid samples, can be found elsewhere<sup>94</sup>.





Figure 2.17 Illustration of the spin echo pulse sequence and the diagram of the evolution of the magnetization vector (red arrows) after the 90° (x) pulse. 'RF' (radiofrequency) and 'acq' (acquisition) represent the pulses and the signal acquisition, respectively. The effect of the 180° (x) pulse is better visualized by separating the vectors in (b) and (c) into their corresponding *x*-and *y*-components (orange arrows). Note that the duration of the 90° and 180° pulses are much shorter than delay time  $\tau$  in practice. The diagrams are adapted from reference<sup>95</sup> with modification.

The spin echo experiment is one of the most useful pulsed NMR experiments, which is often a component of more sophisticated experiments.<sup>95</sup> The pulse sequence for the spin echo experiment and the effect of the 180 ° pulse on a magnetization vector in the transverse plane are illustrated in Figure 2.17. The 90 ° (x) pulse places the bulk magnetization over the sample along the –y-axis. During the first time delay of  $\tau$ , the vector precesses from –y- to x-axis with a phase evolution of  $\phi$ . Then the 180 ° (x) pulse brings the vector from its original place to the

mirror image position around the *x*-axis. After the second time delay of  $\tau$ , the vector evolves to a position aligned along the *y*-axis forming an echo, since the evolution prior to the echo is perfectly reversed after the 180 pulse. From this point on, the magnetization precesses around the *z*-axis (direction of the magnetic field) in a FID. During the precession process, the fluctuating magnetic field induces a current in the coil that is wound around the *y*-axis. This current is then amplified and recorded as the NMR signal (Figure 2.16b).

### 2.3.2.3 Cross Polarisation (CP)

The CP experiment is commonly performed to improve the sensitivity of the NMR measurement by transferring the magnetization from an abundant spin species (<sup>19</sup>F) with large magnetic moment to a relatively insensitive nucleus (<sup>13</sup>C) with a low magnetic moment. The experiment requires the two nuclei to be dipolar coupled to one another, that is, in close proximity. For that reason, it can also be employed to verify the chemical bond/spatial proximity between the two atoms. In this thesis work, the CP experiment was used to detect the minor impurity phase,  $CF_x$ , formed during the ball-mill process from the reduction of  $CuF_2$  in the presence of carbon.



Figure 2.18 Diagram of a <sup>19</sup>F-<sup>13</sup>C CP pulse sequence. A 90  $^{\circ}(x)$  pulse is only applied to the 19F channel and the signal is acquired on the <sup>13</sup>C channel.  $\tau_{ct}$ ,  $\tau_{acq}$ ,  $\tau_r$  correspond to the contact time, decoupling period (acquisition time), and relaxation delay, respectively.

The diagram of the pulse sequence for the CP experiment is shown in Figure 2.18. The 90°(x) pulse is only applied to fluorine, which rotates the magnetization from *z*- to -y-axis. The 90° pulse is followed by another long pulse on *y* in order to keep the magnetization along -y-axis, which is called the spin-lock process. While the spin is locked in place, a pulse is applied on the <sup>13</sup>C-channel for an equal period of time, defined as the contact time. The magnetization will be efficiently transferred when the RF fields at the two channels are

matched in intensity. After the contact time, an irradiation is applied to decouple the <sup>19</sup>F from the <sup>13</sup>C nuclei while their signal is recorded.



### 2.3.2.4 Saturation Recovery (SR)

Figure 2.19 Diagram of the SR pulse sequence and the illustration of the evolution of the magnetization vector. The  $T_1$  is derived by fitting the curve of the integrated area of the resonances as a function of recovery times using Equation 123.

The aim of the SR experiment is to measure  $T_1$ , which is called the spin-lattice relaxation time. The spin-lattice relaxation is a process to redistribute the populations of individual spin states back to their thermal equilibrium distribution after perturbation, such as and RF pulse. The process is monitored by measuring the recovery of the *z*-component of the bulk magnetization vector which usually follows an exponential function. As suggested by its name,  $T_1$  relaxation involves an interaction of the nuclear spins with their surroundings, the lattice. It depends on the presence of magnetic interactions that are modulated by dynamic processes in the lattice at the right time scale. In the presence of a conductive surface, the interaction between the nuclear spin and the conduction electrons is stronger for the spins that are in close proximity to the surface and it scales with the distance from it. Thus it is expected that the  $T_1$  relaxation time will increase for spins that are further away from a conductive surface. As such, the evolution of the  $T_1$  relaxation time can be used to monitor indirectly the change in particle size. The details of the relaxation mechanism is beyond the scope of this thesis, but can be found elsewhere<sup>92</sup>. The SR pulse sequence consists of a train of 90 ° (x) pulses, followed by a recovery period with various delay times. Then another 90 ° (x) pulse is applied before the acquisition. The recovery times are normally sorted as an array in an ascending order,  $\tau_1$ ,  $\tau_2$ ,... $\tau_n$ . As illustrated in Figure 2.15, the bulk magnetization vector of the sample is initially aligned along the *z*-axis. The train of 90 ° (x) pulses is optimized to saturate the spin system, that is to set M<sub>*z*</sub> = 0. During the relaxation period, the bulk magnetization gradually recovers and reaches its equilibrium value. The magnitude of the signal after each delay is measured following the last 90 ° pulse and depends on the recovery time  $\tau$ . The signal intensity (or area) follows an exponential function,

$$y = y_0 \left( 1 - e^{\frac{\tau}{T_1}} \right),$$
 (123)

where  $y_0$  corresponds to the maximum intensity. Thereby  $T_1$  can be evaluated by fitting the plot to the equation.

# 3 Local Structure Investigation of $Li_{1+x}V_{1-x}O_2$

# 3.1 Introduction

Layered oxide materials such as LiCoO<sub>2</sub>, LiNiO<sub>2</sub> and LiVO<sub>2</sub> and their substituted variants have been widely studied as potential insertion electrodes for lithium-ion batteries<sup>96-99</sup>. Amongst this diversity of layered materials,  $Li_{1+x}V_{1-x}O_2$  stands out for the reason that the Li insertion takes place at very low voltage (~ 0.1 V) with a theoretical volumetric capacity of 1,360 mAh/cm<sup>-3</sup> (vs. 790 mAh/cm<sup>-3</sup> for graphite), and may thus find use as a practical anode material<sup>100-101</sup>.

# 3.1.1 Prior Knowledge of the Structure of LiVO<sub>2</sub>



Figure 3.1 Schematic view of the V local displacements in the proposed trimers. Red balls denote the V positions in an undistorted structure (z = 0), the blue dashed line represents the original rhombohedral lattice and the green dashed line represents the superlattice. The purple arrows indicate the displacements of the V<sup>3+</sup> ions starting with a V<sup>3+</sup> ion at (0 0 0) in the undistorted lattice. The V<sup>3+</sup> ions shift towards the center of a triangle (thick black line) forming a cluster. The red arrows show the directions of the other five possible displacement of a certain V<sup>3+</sup> ion, suggesting 6 possible arrangements of V trimers in each layer.

Stoichiometric LiVO<sub>2</sub> crystallizes in an ordered rocksalt–related  $R\overline{3}m$  structure with Li<sup>+</sup> and V<sup>3+</sup> occupying alternating (111) planes (Figure 3.1). The material has been the study of numerous previous investigations primarily on the basis of its magnetic properties,<sup>102-103</sup> the presence of a 2D triangular lattice of V<sup>3+</sup>  $3d^2$  ions together with antiferromagnetic exchange coupling leading to geometrical frustration.<sup>104</sup> The frustration is partially alleviated by the formation of clusters composed of singlet V<sup>3+</sup>–V<sup>3+</sup>–V<sup>3+</sup> trimers at ambient temperature, the V

ions experiencing small co-planar shifts from their ideal positions toward the center of a mutually defined triangle, as illustrated schematically in Figure 3.1. The spin–singlet trimerisation is driven by orbital ordering and polarisation amidst the three  $V^{3+}$  t<sub>2g</sub>( $\uparrow\uparrow$ ) manifolds in each triangular unit<sup>105-107</sup>. A superlattice structure results, characterized by a (1/3 1/3 0) reflection (with indexing based upon the original  $\alpha$ –NaFeO<sub>2</sub> type cell, see Appendix 1) observed by X-ray<sup>10,13</sup> and electron<sup>11</sup> diffraction. On heating, a first order phase transition is observed accompanied by considerable hysteresis (the critical temperature, T<sub>c</sub>, is ~500 K on heating and ~400 K on cooling). This material is essentially diamagnetic below T<sub>c</sub>, behaving as a Curie-Weiss paramagnet above this temperature<sup>108-110</sup>.

#### 3.1.2 Motivation of the Study

A previous study has shown that the Li-excess material  $Li_{1.07}V_{0.93}O_2$  exhibits much better electrochemical performance than the stoichiometric material LiVO<sub>2</sub>, which does not readily insert additional Li (Figure 3.2a). A structural study of the  $Li_{1+x}V_{1-x}O_2$  series via the laboratory XRPD (Figure 3.2b) revealed no apparent differences with respect to the average structures between different compositions, indicating the local structure governs the electrochemical behaviour.<sup>11</sup>



Figure 3.2 (a) Potential curves for the  $Li_{1+x}V_{1-x}O_2$  series and (b) the corresponding lab XRPD patterns (x = 0, black; x = 0.03, red; x = 0.07, purple). Both figures are adapted from the reference<sup>11</sup>.

The main goal of this study is to provide a detailed characterization of the Li and V local environments occurring in the stoichiometric and Li-excess materials, and to correlate such observations with the electrochemical performance. PDF analysis and MAS NMR spectroscopy are mutually complementary methods by which to study the local environments occurring in the present system. While the X-ray PDF method is used here for the study of the local rearrangements involving V sites, it is less effective for Li-centered distortions due to

the strong dependence of X-ray scattering power on atomic number (Equation 37). Insight into Li environments nevertheless remains a key target of the present study, given that the Li ions are directly involved in the electrochemistry of the material, and is provided here directly by MAS NMR.

# 3.2 Experimental

# 3.2.1 Materials Preparation

Li<sub>1+x</sub>V<sub>1-x</sub>O<sub>2</sub> samples were prepared by collaborator, Dr. Paul Adamson from University of St. Andrews. They were synthesized by the reaction of Li<sub>2</sub>CO<sub>3</sub> and V<sub>2</sub>O<sub>3</sub> in the molar ratio 1+*x*:1-*x*. Dried Li<sub>2</sub>CO<sub>3</sub> (Aldrich, 99%) and V<sub>2</sub>O<sub>3</sub> (Aldrich, 99+%) powders were mixed together in a MBraun argon-filled dry box with a combined O<sub>2</sub> and H<sub>2</sub>O content of less than 1 ppm. <sup>6</sup>Li<sub>1+x</sub>V<sub>1-x</sub>O<sub>2</sub> samples were prepared in the same way using <sup>6</sup>Li<sub>2</sub>CO<sub>3</sub> (Cambridge Isotope Laboratories, 95%). The mixture was placed in a gas-tight container (sealed with a cork gasket) and ball milled for 90 minutes (SPEX Centri-Prep 8000 M mixer/mill). The container was returned to the dry box and the powder transferred into an alumina crucible, which was covered with a lid. The mixture was then heated at 800 °C for 10 hours under flowing argon (BOC). Once cooled to room temperature the compound was ground by hand in air and heated at 850 °C for 12 hours under flowing 5% hydrogen in argon (BOC)<sup>111</sup>.

# 3.2.2 NMR Spectroscopy

The NMR studies presented in this chapter were performed by my coworker, Dr. Fr él érique Pourpoint. <sup>7</sup>Li NMR experiments were conducted using rotor synchronized spin echo experiments with an evolution and refocusing period of one rotor cycle and a 1.8 mm probe designed by A. Samoson (spinning frequency = 35 kHz) on a 4.7 T Chemagnetics magnet. The  $\pi/2$  pulse length was 1.38 µs. <sup>6</sup>Li NMR spectra were recorded on a 9.4 T Bruker magnet using an Avance II console and a 4 mm probe. Rotor synchronized Hahn echo experiments (spinning frequency = 14 kHz) were used with one rotor cycle of evolution/refocusing. The  $\pi/2$  pulse length was 4.50 µs. A POST-C7 sequence<sup>112-113</sup> was implemented using a spinning speed of 8 kHz, with 16 scans in the direct dimension. Double quantum (DQ) evolution times of 17.5 and 12.25 ms were used for LiVO<sub>2</sub> and Li<sub>1.07</sub>V<sub>0.93</sub>O<sub>2</sub>, respectively. Spin echo experiments were recorded using a recycle delay of 10s while the 2D experiments used 100s and 5s for LiVO<sub>2</sub> and Li<sub>1.07</sub>V<sub>0.93</sub>O<sub>2</sub>, respectively, and were referenced to LiCl 1 M at 0 ppm.

# 3.2.3 X-ray Total Scattering

PDF analyses were performed on synchrotron X-ray total scattering data for pristine LiVO<sub>2</sub> together with samples incorporating 3, 5, 7 and 10% of excess lithium ( $Li_{1,03}V_{0.97}O_2$ )  $Li_{1.05}V_{0.95}O_2$ ,  $Li_{1.07}V_{0.93}O_2$ , and  $Li_{1.10}V_{0.90}O_2$ , respectively). Total scattering data were collected at room temperature using an amorphous Si 2D detector with an X-ray energy of 58 keV (wavelength  $\lambda = 0.21270$  Å) at beamline 11-ID-B at the Advanced Photon Source (APS) at Argonne National Laboratory<sup>114</sup>. The X-ray diffraction experiments were conducted in transmission geometry on finely powdered samples that were sealed in Kapton capillaries filled with argon gas. A CeO<sub>2</sub> standard was used to calibrate the sample-to-detector distance (Figure 2.10) and the tilt of the image plate (IP) relative to the beam path. Scattering measurements for the empty Kapton capillary were also performed under the same experimental conditions in order to obtain the instrumental background<sup>77</sup>. Intensity data versus  $2\theta$  and Q were obtained by converting the integrated IP data using the Fit2D software<sup>115</sup>. The PDF data were generated using the PDFgetX2 program<sup>116</sup>. Data corrections, including background subtraction, sample self-absorption, multiple scattering, X-ray polarisation, and Compton scattering were included in order to obtain the normalized scattering intensity S(Q) (Section 2.1.7.2).<sup>117</sup> The pair distribution function G(r) was generated by direct FT of Q[S(Q) - 1] (Section 2.1.7.3). A  $Q_{\text{max}}$  (Equation 105) of 24.0 Å<sup>-1</sup> was used, representing a tradeoff between the size of the IP and the sample-to-detector distance. Structure refinement and the fitting of G(r) were performed using the PDFgui software<sup>118</sup>. Previously collected scattering data for the Ni standard were processed and refined to obtain the instrumental damping factor. X-ray diffraction analysis was performed with the FullProf software<sup>119</sup>.

## 3.3 Results

# 3.3.1 <sup>6,7</sup>Li NMR

The data presented in this section were collected and processed by Dr. Fr éd érique Pourpoint.

# <sup>7</sup>Li NMR:

<sup>7</sup>Li and <sup>51</sup>V NMR studies have already been performed on the stoichiometric materials  $\text{LiVS}_2^{120}$  and  $\text{LiVO}_2^{121-122}$ , and are apparently sensitive to the V<sup>3+</sup>–V<sup>3+</sup>–V<sup>3+</sup> trimerisation. Recently, Takao *et al.* have attributed the two signals observed in the <sup>7</sup>Li NMR spectra (Figure 3.3) of LiVO<sub>2</sub> at –2.9 ppm ( $\beta_0$ ) and +1.1 ppm ( $\alpha_0$ ) to the different Li environments within the layer caused by the formation of trimers<sup>122</sup> (see Figure 3.13a).



Figure 3.3 <sup>7</sup>Li NMR spectra of  $Li_{1+x}V_{1-x}O_2$  with  $0 \le x \le 0.10$  recorded at 4.7T with a spinning speed of 35 kHz. (Data were collected and processed by Dr. Frederique Pourpoint.)

The local structure occurring in  $\text{Li}_{1+x}\text{V}_{1-x}\text{O}_2$  was initially investigated by <sup>7</sup>Li NMR spectroscopy. First, resonances at approximately 0 ppm are observed in all spectra, in agreement with the previously published <sup>7</sup>Li NMR of  $\text{LiVO}_2^{122}$  and consistent with Li local environments that are not in the vicinity of paramagnetic species, in keeping with the suggested formation of a spin singlet trimerised state. In the non-stoichiometric compounds, the –2.9 ppm signal grows in intensity with an increasing amount of excessive Li. In addition, the "0 ppm" signals become broader and less well resolved, because of an increase in the disorder of the material. Ionic and electronic mobility may also contribute to this broadening. When the inserted Li content reaches 7% ( $\text{Li}_{1.07}\text{V}_{0.93}\text{O}_2$ ), the –2.9 and 1.1 ppm resonances can no longer be separately resolved, a broad signal with a shoulder instead being observed. Meanwhile, only one broad signal is observed in the Li<sub>1.10</sub>V<sub>0.90</sub>O<sub>2</sub> spectrum.

# <sup>6</sup>Li NMR:

The <sup>6</sup>Li and <sup>7</sup>Li isotopes are both NMR-active, <sup>7</sup>Li (nuclear spin quantum number I = 3/2) having a much higher natural abundance (92.5%) than <sup>6</sup>Li (I = 1) (7.5%) and a larger quadrupolar moment (albeit still very small compared with many other quadrupolar nuclei). However, the smaller gyromagnetic ratio of <sup>6</sup>Li ( $\gamma_{7Li}$  / $\gamma_{6Li}$  = 2.6) leads to MAS spectra displaying reduced spinning side band manifolds in paramagnetic phases, and also usually

provides higher resolution spectra due to the combination of a reduction in Li-Li homonuclear interactions with the lengthening of  $T_1$  relaxation time. Therefore, <sup>6</sup>Li NMR was employed in pursuit of better resolved spectra.



Figure 3.4 <sup>6</sup>Li NMR spectra of <sup>6</sup>Li<sub>1+x</sub>V<sub>1-x</sub>O<sub>2</sub> with  $0 \le x \le 0.07$  recorded at 9.4 T with a spinning speed of 14 kHz. Data were collected by Dr. Fr éd érique Pourpoint. (Data were collected and processed by Dr. Fr éd érique Pourpoint.)

Much sharper signals are seen in the <sup>6</sup>Li NMR spectra of <sup>6</sup>Li<sub>1+x</sub>V<sub>1-x</sub>O<sub>2</sub> (Figure 3.4), presumably due to the reduction in the strengths of paramagnetic, quadrupolar and dipolar interactions relative to those observed in the <sup>7</sup>Li NMR. Three resonances at 1.7, -1.4 and -2.9 ppm are now resolved in the spectra of LiVO<sub>2</sub> and Li<sub>1.03</sub>V<sub>0.97</sub>O<sub>2</sub>, the relative intensity of the resonance at -2.9 ppm growing slightly with increasing Li content (see Table 3.1 for details). It is no longer possible to clearly distinguish the three resonances for excess Li contents greater than approximately 5% (Li<sub>1.05</sub>V<sub>0.95</sub>O<sub>2</sub>), suggestive of a more disordered structure and consistent with the observations from <sup>7</sup>Li NMR.

DQ filtered 2D experiments have been recorded for the stoichiometric LiVO<sub>2</sub> and  $Li_{1.07}V_{0.93}O_2$  materials (Figure 3.5) to aid in the assignment of the <sup>6</sup>Li NMR. The experiment should provide correlations between Li nuclei linked by <sup>6</sup>Li homonuclear dipolar couplings, thereby identifying those pairs of nuclei that are both close in space. In general in 2D experiments, correlations between two signals with frequencies  $v_A$  and  $v_B$  will manifest as cross peaks at a position  $v_A + v_B$  in the DQ dimension, the individual signals appearing at  $v_A$  and  $v_B$  in the single quantum dimension. Off-diagonal cross peaks are clearly present in

LiVO<sub>2</sub> between the two signals at 1.7 and -2.9 ppm, suggesting that the two sites producing these resonances are in close proximity, likely in the same Li layer (Figure 3.5a). The separations between Li ions in the same and neighboring layers are 2.83 and 5.20 Å, respectively. In contrast, the only correlations involving the resonance at -1.4 ppm appear on the diagonal, indicating that these sites are close only to other ions of the same type. In contrast, only very weak cross peaks are seen in the 2D spectrum of Li<sub>1.07</sub>V<sub>0.93</sub>O<sub>2</sub> (Figure 3.5b). The spectrum is dominated by peaks along the diagonal, the main peak corresponding to the correlation involving the -1.4 ppm signal. There is a slight distortion in the spectrum that acts to rotate the positions of the cross peaks, the origin of which remains undetermined.



Figure 3.5 2D spectra recorded at 9.4 T with a spinning speed of 8 kHz for (a)  $LiVO_2$  and (b)  $Li_{1.07}V_{0.93}O_2$ . The dashed line shows the cross peak between two peaks. The solid lines show the diagonal connecting peaks in the single quantum (SQ) and double quantum (DQ) dimensions. The "\*" sign in (a) marks artifacts due to truncation in the indirect dimension. (Data were collected and processed by Dr. Fr éd érique Pourpoint.)

### 3.3.2 Bragg Diffraction via X-ray Total Scattering

The Bragg diffraction patterns (strictly, the total scattering data) of the Li<sub>1+x</sub>V<sub>1-x</sub>O<sub>2</sub> samples, collected with synchrotron X-ray diffraction and subsequently converted to the  $2\theta$  values corresponding to Cu K $\alpha_1$  radiation are shown in Figure 3.6. The experimental data are compared with the calculated diffraction pattern of the undistorted LiVO<sub>2</sub> phase (*i.e.*, the  $R\bar{3}m$  symmetry  $\alpha$ -NaFeO<sub>2</sub> structure<sup>111</sup>). The experimental data are in excellent agreement with this simulated pattern, indicating that the undistorted model provides a good model for the long range structure. However, a weak reflection emerges at around  $2\theta = 21^{\circ}$  in the patterns of all the samples, and a broad feature between  $2\theta = 18^{\circ} - 30^{\circ}$  along with two other weak peaks at around  $2\theta = 28^{\circ}$  and  $32^{\circ}$  was observed for Li<sub>1.10</sub>V<sub>0.90</sub>O<sub>2</sub>. Comparing these patterns with the

XRPD pattern simulated using the distorted  $LiVO_2$  superstructure (Figure 3.9) containing V trimers (Section 3.4.1), these weak peaks seem to be the superlattice reflections for  $Li_{1+x}V_{1-x}O_2$ , as previously discussed by Onoda and Tian<sup>109-110</sup> (Figure 3.6, green pattern). However, they are not detected by the laboratory XRD (Figure 3.2b), which is probably due to a short coherence length of the superstructure, or a lower X-ray flux from the laboratory diffractometer than that from a synchrotron source.



Figure 3.6 Experimental synchrotron XRD patterns for the  $\text{Li}_{1+x}\text{V}_{1-x}\text{O}_2$  series. The possible superlattice reflections are marked with asterisks. Two simulated patterns for LiVO<sub>2</sub> are shown below, where the black pattern is simulated from the rhombohedral ( $R\overline{3}m$ ) structure and cell parameters reported by Armstrong *et al.*<sup>111</sup> and the green pattern is simulated from the refined superlattice structure (extracted from PDF data, Figure 3.9). This structure is constructed based on the superlattice model proposed by Takao *et al.*<sup>122</sup>.

## 3.3.3 X-ray PDF Analyses

PDF analysis of the synchrotron total scattering data is plotted in the ranges from 0 to 18 Å and from 18 to 60 Å in Figure 3.7a and b, respectively, similar plots being observed for all samples. The PDF pattern simulated using the undistorted LiVO<sub>2</sub> structure ( $R\overline{3}m$  symmetry with cell parameters a=2.8377 Å, c=14.8230 Å<sup>111</sup>) is very similar to the experimental profiles, if attention is restricted to intermediate-to-long range (*i.e.* greater than approximately 6 Å). However, some noticeable discrepancies are observed between the experimental and simulated profiles in the short (from approximately 2 to 6 Å) range. In particular, the peak in the simulated profile at 2.8 Å corresponding to the first-shell V-V interatomic distance (marked B in Figure 3.7a) does not occur in all of the experimental patterns, and is replaced by two new peaks at 2.5 and 3.0 Å (marked D and E respectively in Figure 3.7a), consistent with the presence of V trimers<sup>122</sup>.



Figure 3.7 PDF analyses of  $\text{Li}_{1+x}\text{V}_{1-x}\text{O}_2$  plotted in the r-range of (a) 0 – 18 Å, and (b) 18 – 60 Å. The pair correlations in (a) labelled with A and C and the weaker features F correspond to V-O interatomic correlations while B, D and E correspond to V-V interatomic correlations. The experimental PDFs are compared to those calculated with the  $\text{LiVO}_2$  rhombohedral structural model reported by Armstrong *et al.*<sup>111</sup>

In the absence of trimerisation, the six coplanar V-V interatomic separations per V site would be of equal length, while the presence of trimers leads to a displacement of each V cation to form two shorter and four longer coplanar V-V separations<sup>122</sup> with a predicted intensity ratio of 1:2, all of the latter being in good agreement with experimental findings. Furthermore, rather than a peak at approximately 3.5 Å corresponding to V-O separations in the second coordination shell of the undistorted V cations (marked C in Figure 3.7a), multiple peaks instead emerge in the experimental profiles (in the region marked F) attributable to the

distortions of the  $VO_6$  octahedra due to trimerisation. The displacement of V atoms apparently does not vary significantly with increasing Li content, but there is a reduction in the intensities of the correlations, attributable in part to the decrease in V content.

## 3.4 Discussion

### 3.4.1 Structural Model for LiVO<sub>2</sub>

Both the NMR and X-ray analyses provide clear evidence for local structural distortions persisting throughout the whole  $Li_{1+x}V_{1-x}O_2$  series that are not representable within a simple structural model based on rhombohedral LiVO<sub>2</sub>. Making use of both experimental NMR and PDF, we now construct a model capturing some of the important distortions. We start by considering a single V-layer, constructing a 2D supercell from the undistorted 2D rhombohedral unit cell<sup>111, 122</sup>. The new  $\bar{a}$  and  $\bar{b}$  lattice parameters (green dashed lines, Figure 3.1) are defined by  $\overline{a_r} - \overline{b_r}$  and  $\overline{a_r} + 2\overline{b_r}$  respectively, where  $\overline{a_r}$  and  $\overline{b_r}$  are the lattice parameters of the original rhombohedral cell (blue dashed lines, Figure 3.1). The P1 space group is used hereafter for its flexibility in the representation of the V distortions in the subsequent analysis and for the reason that it simplifies the analysis in three dimensions. The displacement model was constructed by assuming that each V<sup>3+</sup> ion shifts towards the center of a triangle formed by three  $V^{3+}$  ions, forming trimers within the (001) V planes, as shown in Figure 3.1. A magnitude 0.17 Å of the displacement of each  $V^{3+}$  cation was extracted from a simple geometrical calculation on the basis of the 1<sup>st</sup> coordination shell V-V interatomic distances (atomic pairs D and E) observed in the PDF patterns (Figure 3.7a), which correspond to the intra- (D) and shortest inter-trimer (E) V-V distances. Proceeding on the assumption that the local distortions of the  $V^{3+}$  ions are homogeneously distributed throughout each (001) V layer, specification of the direction of displacement of one  $V^{3+}$  ion suffices to determine the positions of all remaining  $V^{3+}$  ions within the same layer. Given that each  $V^{3+}$  has six possible displacement vector orientations (the six red arrows shown in Figure 3.1), six possible (symmetry related) arrangements of the trimer clusters emerge within each layer, relative to the positions of  $V^{3+}$  ions in a notionally undistorted 2D layer. The six possible arrangements become important only when we consider the 3D packing of V layers along the hexagonal *c*-axis, generating six distinct stacking arrangements in a two V-layer supercell and 36 in a three V-layer cell, all as derived from cubic close packing. The latter supercell size provides a significantly greater degree of structural freedom and is used hereafter, leading to 36 distinct unit cells. Clearly, some of these 36 cells are symmetry related, an issue discussed later along with the effect of the Li layer stacking. We note that there is no *a priori* requirement that the packing of the trimer layers should repeat over an interlayer separation consistent with three V layers; many stacking sequences are possible, alongside the chance that the material displays complete structural disorder. However, in order to choose a tractable structural model for the further analysis of the scattering data, a series of preliminary refinements of the 36 candidate cells were performed, fitting to the PDF data for the LiVO<sub>2</sub> sample over distances (*r*-range hereafter) ranging from 1.6 to 10 Å. Given that variations in the local coordination geometries of the V<sup>3+</sup> ions were most evident over short distances (see Figure 3.7a), most of the short range structural information is expected to be reliably captured by these models, albeit that the intermediate to long-range order may not be modeled correctly.



Figure 3.8 Distribution of the R-factors ( $R_w$ ) yielded from PDF structural refinement in short range (1.6 - 10 Å) using the 36 structural models.

The weighted agreement R-factors  $(R_w)^{77}$  (Equation 119) of the structural refinements of the 36 candidate cells varied from 19.96 to 24.25%, 27 of the structural models yielding an  $R_w$  lower than or equal to 20.7% whilst nine yielding an  $R_w$  higher than 22.2% (Figure 3.8). The structure with the lowest  $R_w = 19.96\%$  was adopted as the model superlattice unit cell (Figure 3.9) and its atomic positions are given in Appendix 2; the precise V arrangement and stacking sequence occurring in this cell will be discussed later. The simulated XRD pattern calculated for this superstructure is shown in Figure 3.6 (green pattern). As discussed earlier, the most noticeable additional reflections occur in the range from  $2\theta = 20^{\circ}$  to 35°, while the weak reflection observed experimentally at approximately 21° in all samples seems to be reasonably ascribed to an overlap of the first two additional reflections (Figure 3.6). The two simulated reflections occurring at approximately  $2\theta = 28^{\circ}$  and  $32^{\circ}$  may account for the further two weak reflections that are clearly observed only in the Li<sub>1.10</sub>V<sub>0.90</sub>O<sub>2</sub> sample. The presence of a background feature only for this sample may be indicative of increased disorder.

Note that the structure model discussed in this context only provides a good description of the actual structure in a short range. The actual positions and the relative intensities of those superlattice peaks might correlate with the structure disorder beyond the short *r*-range, *i.e.*, the distribution of the trimers and/or the stacking sequence of the V-layer. Such disorder, if present, should be reflected in the intermediate range of the PDF, which may cause the mismatch in the PDF refinement (in later discussion), and account for the discrepancies between the experimental and simulated superlattice reflections in the XRPD pattern.



Figure 3.9 Supercell structure employed for PDF refinement, in which Li (blue), V (dark green) and O (red) ions occupy alternating (111) planes, ABC-stacking occurring along the c-axis direction.

We use the supercell model derived above to perform a more detailed refinement of the short to long-range structure (from 1.6 to 60 Å) (Figure 3.10). Initially, both the Li and O atomic positions were fixed, refining only the V atom positions. The V displacement parameters within each layer were constrained to be equal, but were allowed to vary between layers. The quality of the fit varied dramatically with *r*-range, resulting in an overall  $R_w = 31.64\%$  for the full 1.6 to 60 Å range. Note that  $R_w$  is higher than above due to the fact that a larger data range is used in the refinements. Good agreement between the experimental and



Figure 3.10 PDF refinement of LiVO<sub>2</sub> (with fixed O atomic position) in the r-range of 1.6 - 60 Å ( $R_w = 31.64\%$ ). Two insets are the zoomed-in regions of 1.6 - 16 Å and 40 - 60 Å, red = calculated pattern, blue = experimental pattern.

calculated pattern is obtained at short range (r-range 1.6 to 16 Å; top inset in Figure 3.10a), whereas significant deviations are noted at longer range (r-range 40 to 60 Å; bottom inset in Figure 3.10b). Taken together, these findings suggest that the local distortions present in the  $V^{3+}$  layers are reasonably well accounted for, but that the long range ordering is not accurately represented. Since the quality of the fit varies significantly with the r-range considered, individual refinements were performed in three distinct r-ranges, namely 1.6 to 16 Å, 16 to 30 Å and 30 to 60 Å, so as to obtain a better understanding of the V distortions. The first range was chosen to capture the inter- and intra-layer correlations, while the third captures the longer-range correlations.

The refinement of the 1.6 to 16 Å data yielded an  $R_w = 22.00\%$  and a slightly better fit to peaks D and E (Figure 3.11a) over that obtained in the refinement shown in Figure 3.10. In addition, the multiple peaks in region F at around 3.5 Å are now captured by the calculated pattern. However, the width of peak A is apparently sharper in the experimental data, suggestive of a less distorted V local environment and a sharper distribution of V-O distances. The refinements of the 16 to 30 Å and 30 to 60 Å data yielded  $R_w = 22.20\%$  (Figure 3.11b) and 25.65% (Figure 3.11c), respectively, which suggests that both the intermediate and long range structure of LiVO<sub>2</sub> can be reasonably well represented by the trimer superstructure.



Figure 3.11 PDF refinement for LiVO<sub>2</sub> (with fixed O atomic positions) in the short, intermediate and long range. (a) 1.6 - 16 Å ( $R_w = 22.00\%$ ). (b) 16 - 30 Å ( $R_w = 22.20\%$ ). (c) 30 - 60 Å ( $R_w = 25.60\%$ ). Peak A and the wiggles, F, correspond to V-O interatomic correlations, D and E correspond to V-V interatomic correlations, red = calculated pattern, blue = experimental pattern.



Figure 3.12 (a) PDF refinement for LiVO<sub>2</sub> (where the O atomic position is now refined) in the range from 1.6 - 16 Å ( $R_w = 10.19\%$ ). (b) The 1.6 - 32 Å and (c) 32 - 60 Å range of the simulated pattern for LiVO<sub>2</sub>, using the structure refinement shown in (a) ( $R_w = 35.13\%$ ), red = calculated pattern, blue = experimental pattern.

The structural data is given in the supplemental data along with the V-O and V-V distances, average values of 2.54(2) and 3.00(2) emerging for the latter, corresponding to V-V separations within and between trimers, respectively. The corresponding displacement magnitudes of V atoms from their normal positions in the ideal  $\alpha$ -NaFeO<sub>2</sub> structure amounts to 0.17(2) Å. In contrast, a simulation of the PDF pattern in the whole r-range from 1.6 to 60 Å, on the basis of the superstructure refined solely from the short range data (as just described) yields a poor fit at intermediate and longer distances with an  $R_w = 35.13\%$  (Figure 3.12b and c). The fit is worst at intermediate ranges (Figure 3.12b), which may be due to variations and increased disorder in the stacking order of the V trimers that are not captured in the structural model. Such effects will be less apparent at longer distances.

# 3.4.2 <sup>6,7</sup>Li NMR Spectral Assignment

material	resonance					
materiar	1.7ppm	-1.4ppm	-2.9ppm			
LiVO <sub>2</sub>	20	51	29			
Li <sub>1.03</sub> V <sub>0.97</sub> O <sub>2</sub>	16.3	46.3	37.4			

Table 3.1 Relative intensities of the three resonances in the  ${}^{6}$ Li NMR spectra (Figure 3.4) for LiVO<sub>2</sub> and Li<sub>1.03</sub>V<sub>0.97</sub>O<sub>2</sub>.

We now use the derived structural model to analyze the NMR data in more detail. The  $V^{3+}$  ion in LiVO<sub>2</sub> has a  $d^2$  electronic configuration and thus, in principle, bears two unpaired electrons. The <sup>6,7</sup>Li NMR spectra of paramagnetic materials typically show broad lineshapes, large hyperfine shifts, and short nuclear relaxation times<sup>123-124</sup>. However, as discussed above, the occurrence in LiVO<sub>2</sub> of antiferromagnetic exchange, and orbital ordering and polarisation leads to the formation of singlet state  $V^{3+}$  trimers<sup>104</sup>, thereby explaining the small chemical shifts around 0 ppm observed in the <sup>6,7</sup>Li NMR spectra, along with the long relaxation time (of a few seconds) and relatively sharp signals. An explanation for the multiple resonances emerges from a consideration of the effects of  $V^{3+}$  trimerisation on the Li local environments. Based on the 2D NMR spectrum of the stoichiometric material, three major local environments can be resolved, where the two giving rise to the 1.7 and -2.9 ppm signals most likely reside in the same layer. The third Li site corresponding to the signal at -1.4 ppm lies further away in the structure from the other two. At least two hypotheses may be proposed: firstly, that the third Li occupies an octahedral site of the nominally  $V^{3+}$  layer, filling a V vacancy; or secondly, that three Li environments occur in the alkali metal layer rather than the two identified previously<sup>122</sup>. The first hypothesis appears unlikely, since the -1.4 ppm resonance corresponds to a significant fraction of the Li content (see Table 3.1).

To explore the second hypothesis, the possible Li environments resulting from trimerisation are now considered (Figure 3.13). Considering first a single V<sup>3+</sup> layer, Li may be stacked in the layer(s) above and below so as to yield two different sets of local environments. In Figure 3.13a, one Li lies directly above a trimer (*i.e.*, above the face of the trimer), while two do not (and are, instead, corner-shared with three trimers); these environments are labeled as Li(1f) and Li(3c), respectively. These are the environments considered in reference<sup>122</sup>. Figure 3.13b illustrates the second configuration, in which no Li ions lie above a trimer: instead they are edge-and corner-sharing, resulting in a single environment Li(1e1c), assuming a random arrangement of Li relative to the V layers. If a second V layer is placed above the Li layer, further possible Li environments occur. Figure 3.13c corresponds to the arrangement shown in Figure 3.13a, but incorporating a second V layer placed so that one Li now shares faces with two trimers, while the other two Li ions are corner-sharing with six trimers, resulting in a single Li(2f) and two Li(6c) environments. The probability that this arrangement occurs is 1/12 [derived as  $C_3^1/(C_6^1C_6^1)$ ], where  $C_3^1$  denotes a binomial coefficient].

Table 3.2 The different Li configurations generated by the 4 stacking sequences C - F, shown in						
Figure 3.13. The probability that each configuration occurs, assuming a random stacking of						
vanadium layers, is shown for each stacking sequence and then for each configuration.						

Fig	gure		Li Environment		Probability		
C		Li(2f)			1/36		
	C	Li(6c)			2/36		
D		Li(1f,3c)			4/36		
		Li(6c)			2/36		
Е		Li(1e1c, 1f)			6/36		
		Li(1e1c, 3c)			12/36		
F		Li(1e1c, 1e1c)			9/36		
Li Environment	Li(2f)	Li(6c)	Li(1f,3c)	Li(1e1c, 1f)	Li(1e1c, 3c)	Li(1e1c, 1e1c)	
Probability	1/36	4/36	4/36	6/36	12/36	9/36	

Figure 3.13d shows a second stacking sequence formed from that shown in Figure 3.13a, but here arranged such that the trimers stack above Li ions that do not share faces with the trimers in the other V layer. This arrangement occurs with a probability of  $1/6 [(C_3^1 C_2^1)/(C_6^1 C_6^1)]$  and results in two Li(1f, 3c) and a single Li(6c) environment. The stacking in Figure 3.13e with probability  $1/2 [(C_6^1 C_3^1)/(C_6^1 C_6^1)]$  is formed from the stacking sequences shown in Figure 3.13a and b, and hence face-, edge- and corner-sharing environments result, namely a

single Li(1e1c,1f) and two Li(1e1c,3c). A final arrangement with a probability of 1/4  $[(C_3^1C_3^1)/(C_6^1C_6^1)]$  may be formed from stacking based on Figure 3.13b only, resulting only in Li ions that edge- and corner-share with trimers, namely three Li(1e1c, 1e1c) environments. The probabilities with which each of these different environments occur are summarized in Table 3.2.



Figure 3.13 Projections along the [001] direction shown to demonstrate the different stacking arrangements of the vanadium layers and the resulting Li configurations. The grey hexagonal lattice and blue trimers denote the V positions in the first layer. The dark hexagonal lattice and the green timers represent the 2nd V layer. Red dots denote the Li positions between the two V layers. The three numbers indicate the different Li environments. (a) and (b) illustrate the two possible stacking sequences of a single vanadium layer and the next Li layer. Only (a) results in face sharing of lithium with the vanadium trimers. A second vanadium layer can then be stacked on either (a) or (b) to create stacking sequences (c) – (f).

Eighteen stacking sequences from amongst the total of 36 originally tested in the initial PDF structural refinements yield  $R_w$  values lower than or equal to 20.2% (Figure 3.8), and all contain stacking sequences comprising only arrangements D, E and F with varied stacking order. The structure employed as the initial model for PDF structural refinement was simply chosen based on its low  $R_{\rm w}$ . However, this does not have a significant difference regarding the stacking sequence of V layer in comparison with the other seventeen. Nine stacking sequences with  $R_w$  values around 20.5% only comprise arrangement E. The other nine stacking sequences with  $R_w$  higher than 22.2% comprise arrangements C, which contains trimers stacked directly on top of each other, with Li ions sandwiched in the intervening layer. This is likely to be the least favorable arrangement on energetic grounds as a consequence of the large electrostatic repulsions between the like-charged Li and V cations, consistent with the lack of clear-cut evidence for this stacking sequence in the PDF analyses. Regardless the differences in the V local structure coming from those different stacking sequences, the superlattice reflections of all models are expected to show up at the same  $2\theta$  degree, however, with slightly different relative intensity. Removing the environments generated by sequence C from our analysis, only three Li environments with probabilities of greater than or equal to 16.6% remain (note that the Li environments generated by arrangement C contribute only 8.3% of the total number of Li ions, assuming random stacking). We tentatively assign the environment Li(1e1c, 1e1c) to the resonance at -1.4 ppm since this configuration occurs alone in stacking arrangement F, which is in agreement with the proximity of Li sites in the 2D NMR experiment, and also has a higher probability of 25%. The other major environments Li(1e1c,1f) and Li(1e1c,3c) occur with probabilities of 16.6 and 33% and are assigned to the resonances at 1.7 and -2.9 ppm, respectively, on the basis of the weaker intensity of the resonance at 1.7 ppm and the fact that former environment shares faces with a trimer, likely leading to a shift that will be more distinct from the other two. Both of these environments originate in configuration E, consistent with the cross-peak observed between the 1.7 and -2.9 ppm peaks in the 2D NMR spectrum of LiVO<sub>2</sub> indicative of the spatial proximity of the two originating environments. The other environment found in sequence D that occurs with significant probability (11.1%) is Li(1f,3c). This should give rise to a shift similar to that for Li(1e1c, 1f) and it is likely that the resonances from these two environments overlap, resulting in the higher intensity of this apparently single resonance. The sum of the probabilities for Li(1f, 3c) and Li(1e1c, 1f) (environments) amounts to 10/36 = 27.8%assuming random stacking of the layers. This calculated intensity is higher than observed, again suggesting non-random stacking, and that face-sharing environments are energetically disfavored.

The relative intensities of <sup>6</sup>Li signals arising from the three components do not change significantly on increase of Li content (Figure 3.4), save for a small decrease in the intensity of the Li(1e1c, 1e1c) resonance at 1.4 ppm and a considerable overall broadening of the <sup>6</sup>Li NMR spectra. No distinct resonance is observed that might be assigned to Li ions residing in the  $V^{3+}$  layers, the presence of which has been suggested by previous neutron diffraction<sup>111</sup>. Li substitution into the V layers of  $Li_{1+x}V_{1-x}O_2$  results in an increase in V oxidation state in a notional  $Li_{1+x}V^{4+} 2_{x}V^{3+} O_{2}$  stoichiometry. The present PDF results show that the trimer motif is still present in materials bearing even the highest Li contents, despite the fact that such materials must contain substantial concentrations of  $V^{4+}$  cations (e.g. the average vanadium oxidation state at x = 0.1 is  $V^{3.29+}$ ). One possibility is that  $V^{3+}-V^{3+}-V^{3+}$  trimers may be replaced by  $LiV^{4+}$  clusters, minimizing the disruption of the trimers at even the highest Li substitution levels. Such  $LiV_{2}^{4+}$  clusters should result in  $V_{2}^{4+}-V_{2}^{4+}$  contacts. However such contacts will be present at very low concentrations and will be difficult to detect in the PDF patterns. It is nevertheless surprising that no distinct resonances originating from Li nearby V<sup>4+</sup> cations (either in the V or Li layers) are observed, given that distinct resonances are observed for the Li-deficient  $Li_{1-x}V_{1+x}O_2$  materials, which also contain  $V^{4+}$  cations. Possible explanations for this include mobility of the Li<sup>+</sup> ions, consistent with the much weaker Li correlations seen in the 2D spectrum of Li<sub>1.07</sub>V<sub>0.93</sub>O<sub>2</sub> and/or mobility of the electrons, resulting in a partial or complete averaging of the effective V oxidation state. Both phenomena might result in the broadening of the spectra that is observed experimentally. Magnetic coupling between the  $V^{4+}$  d<sup>1</sup> ions to produce a singlet dimer is certainly also possible. The proposed increase in Li<sup>+</sup> mobility in the Li-excess phases is consistent with their improved electrochemical performance.

# 3.5 Conclusions

PDF analysis of the synchrotron X-ray total scattering data for a series of  $\text{Li}_{1+x}\text{V}_{1-x}\text{O}_2$  samples provides clear evidence for the formation of  $\text{V}^{3+}-\text{V}^{3+}-\text{V}^{3+}$  trimers even in the most lithiated compound studied here (x = 0.1). V-V correlations at 2.54(2) and 3.00(2) Å are observed, which may be regarded as characteristic signatures of trimer formation given that they correspond to V-V distances within and between the trimers, respectively. Such V-V distances correspond to a displacement of the V atoms by 0.17(2) Å from the normal sites of the undistorted  $\alpha$ -NaFeO<sub>2</sub> lattice. A structural model was derived which captured the local distortions of both the V and O atoms. Refinements showed that stacking sequences of the V layers favored arrangements with fewer Li ions located directly above or below (*i.e.*, facesharing) the V trimers. The NMR spectra of these samples confirmed that the V display a strong magnetic ordering to form a diamagnetic S = 0 spin state, again consistent with previous theories of trimer formation<sup>104</sup>. Three dominant <sup>6</sup>Li signals are observed that are assigned to the different environment resulting from the stacking of the trimer-containing layers along the hexagonal *c*-axis, the results again suggesting that local arrangements minimizing the number of Li ions face-sharing with trimers are favored.

# 4 Morphology Study of the TiO<sub>2</sub>-B Nanoparticles

# 4.1 Introduction

TiO<sub>2</sub> has received growing interest due to its promising electrochemical performance compared to the carbon anode<sup>34</sup>: i) various polymorphs of TiO<sub>2</sub> have high theoretical capacities, among which the bronze (B) phase (Figure 4.1) achieves the highest capacity of about 335 mAh/g, comparable to that of graphite (372 mAh/g); ii) as an oxide, TiO<sub>2</sub> has twice the density of graphite, therefore twice the theoretical volumetric energy density; iii) operating voltage of TiO<sub>2</sub> is around 1.6 V (vs. 0 V for graphite), consequently it is safer than graphite under high cycling rates (see Section 1.2.2). More importantly, the existence of various polymorphs of TiO<sub>2</sub> has spurred intensive research in structure engineering.

# 4.1.1 Advantages of Using TiO<sub>2</sub>-B as an Anode for LIBs



Figure 4.1 TiO<sub>2</sub>-B structure illustrated using (a) a ball-stick and (b) a polyhedral model. Both models are comprised of two unit cells (C2/m) whose lattices are shown with blue dashes. Li sites are coloured as pink, green and orange, corresponding to A1, A2, and C sites, respectively. In particular, C sites are in the channels along the *b*-axis.

The best overall performance to date for TiO<sub>2</sub>, taking into account the reversibility, capacity retention and rate capability, has been found in the nanoparticulate bronze (B) phase with an average size of 3 nm.<sup>35</sup> The surface area increases upon nanosizing the particles, leading to a larger interface for Li<sup>+</sup> incorporation and a shorter path length for electronic/ionic transport<sup>32</sup>. In addition, the unique channel structure of the B phase (*C*2/*m*) (see Figure 4.1b) provides low-energy Li<sup>+</sup> pathways from surface to subsurface sites, which is believed to contribute to the pseudocapacitive behaviour<sup>125</sup>. As a result of the nanoscale open-crystal structure, TiO<sub>2</sub>-B retains good capacity at an exceptionally high cycling rate compared to its counterparts.<sup>35</sup>

# 4.1.2 Motivation of the Study

Recently, a method utilizing Debye formula coupled with Monte Carlo-based optimization has been used to model the  $TiO_2$ -B nanoparticles, where the anisotropic peak broadening of the Bragg reflections of the laboratory XRPD data was studied and a prolate ellipsoid structure with c-axis as the major axis was proposed. Nonetheless, the Bragg diffraction analysis of nanomaterials often encounters technical challenges arising from the nature of the diffraction technique and the limited particle sizes. In addition, the information obtained is limited to the long-range structure, while the short-range structure that is sensitive to particle morphologies (see Figure 2.11) and often deviates from the average has been thus far overlooked.

An alternative to the reciprocal-space approach using Bragg diffractions is the pair distribution function (PDF), which is a real-space method utilizing the total scattering, including both Bragg reflections and diffuse scattering. It enables researchers to obtain precise structural information on an atomic scale. For previously reported PDF analyses of nanoparticles, assuming a spherical particle shape has been a common practice for the structure refinement<sup>126</sup>. When the particles have complicated morphologies, structure modelling and data simulation needs to be implemented. Small-angle X-ray scattering (SAXS) is the most sensitive approach for acquiring mesoscale nanoparticle characteristics, including particle size and shape, which is essential information for constructing an accurate structure model.

In the following sections, a detailed method will be presented employing SAXS and PDF analyses, making use of the prior qualitative transmission electron microscopy (TEM) result<sup>35</sup>, in combination with the XRPD data, to study the morphology and the structure of nanoparticles, and finally to attain a representative model that agrees with the experiments in both short- and long-range order. We demonstrate that the TiO<sub>2</sub>-B nanoparticles can be modelled as oblate ellipsoids with the minor axis along the *b*-axis, instead of the reported prolate ellipsoid<sup>127</sup>.

# 4.2 Experimental

### 4.2.1 Materials Preparation and Laboratory Characterization

TiO<sub>2</sub>-B nanoparticles were prepared via hydrothermal methods, and were provided by collaborator, Mr. Z. Liu, from the University of St. Andrews. In the synthesis<sup>35</sup>, 0.72 g of Ti (99.7%) was dissolved in an aqueous solution of  $H_2O_2$  (70 mL, 30.0%) with NH<sub>3</sub> (20 mL, 35%) in an ice-water bath. Then 1.71 g of glycolic acid (99%) was added to the solution
which was then kept at 80°C for several hours to eliminate excess  $H_2O_2$  and  $NH_3$ . Upon mild heating, the solution transformed into a yellow gel, which was later dissolved in water with addition of  $H_2SO_4$  (98.0%) until the pH value of the solution reached 1. The resulting solution was sealed in a Teflon-lined stainless steel autoclave and heated at 160°C for 30 min. After being cooled to room temperature, the solid deposits were separated from the solution by centrifugation, and washed several times with water and ethanol to remove the residue acid. The solid products were then dried at 60 °C over night and calcined at 300 °C for 1 h in dry air, and finally stored in an Ar-filled glove box. The as-prepared nanoparticles were characterized by TEM (JEOL JEM-2110) and wide-angle XRPD (Stoe STADI P diffractometer operated in transmission mode with Fe K $\alpha_1$  radiation,  $\lambda = 1.936$  Å). The acquired diffraction and TEM data are provided by Mr. Z. Liu, in which the XRPD pattern was converted with a Cu K $\alpha_1$ radiation ( $\lambda = 1.541$  Å) for easy comparison with the literature. The simulation of XRPD pattern from a nanoparticle model was performed using the Debye equation (Equation 53) (see Section 2.1.6.4 for details).

### 4.2.2 Small-angle X-ray Scattering

SAXS data were recorded at beamline 12-BM at the Advanced Photon Source, operating at an X-ray energy of 12 keV ( $\lambda = 1.033$  Å) using a MarCCD165 detector. The measured *Q*-range was 0.014 – 0.4 Å<sup>-1</sup>. The sample was sealed in quartz capillary (Ø 1.5 mm) prepared under Ar atmosphere. SAXS data were analyzed using the *Modeling II* tool of the Irena package within IGOR Pro<sup>57</sup>. The Schulz–Zimm distribution<sup>128</sup> of the particles with an interference structure factor<sup>129</sup> was applied (see Section 2.1.5.3 for details in SAXS Data Analysis).

# 4.2.3 X-ray Total Scattering

X-ray total scattering data were collected at beamline 11-ID-B at the APS using an amorphous Si 2D detector with an X-ray energy of 58 keV ( $\lambda = 0.2127$  Å). The experiments were conducted in transmission geometry on a powdered sample that was sealed in a Kapton capillary (Ø 1.0 mm) under Ar atmosphere. The measurements, including a CeO<sub>2</sub> sample as reference and an empty Kapton capillary for data background, were also performed under the same experimental conditions. Data reduction and normalization were performed in the same manner as in other ex situ PDF experiments (see Section 3.2.3). Specifically, a Qmax of 25.0 Å<sup>-1</sup> was used for the PDF extraction. The real-space least-squares refinement and PDF simulations (see Section 2.1.7.5 for details) were performed using the PDFgui<sup>76</sup> and DISCUS<sup>65</sup> software, respectively.

# 4.3 Structure Modelling

In this chapter, the structures modelled for further XRPD and PDF simulations include spheres, and prolate and oblate ellipsoids. The aspect ratios for prolate and oblate ellipsoids were extracted through SAXS data analysis, as discussed later (Section 4.4.2).

To construct a sphere model, a big 3D "box" composed of stacks of repeated unit cells needs to be created first. It is also required that the origin be translated to the centre of the box. A spherical structure model can be obtained by removing all the atoms that have larger distances than "r" from the origin, where r is the radius of the sphere. To construct prolate ellipsoids, the 3D box is firstly contracted by 1/v (where v is the desired aspect ratio, see Figure 2.7) along any of the *a*-, *b*- or *c*-axis of the unit cell. The compressed box is followed by being shaped to a sphere using the  $r_{major}$  of the prolate as the sphere radius. The prolate model can be attained by stretching the sphere by v along the same direction as the prior contraction. Modelling oblate spheroids is done in a similar manner to modelling prolate structures, apart from the stretching and contracting procedures are in reverse order.

Note that the contraction and stretching procedures are performed along the directions of the unit cell lattices, which dictates the elongation and contraction directions of the prolate and oblate spheroids. As a result, the non-right angle,  $\beta$ , in the monoclinic unit cell of the bronze phase (*C*2/*m*) leads to a tilted prolate (model 1 in Figure 4.2) or oblate structure when the elongation or contraction direction is along *c*-axis. To avoid the deviation from a perfect spheroid model (model 2 in Figure 4.2), the monoclinic unit cell (*C*2/*m*) was thereby transformed to a pseudo-orthorhombic cell (*P*1) (with symmetry discarded) prior to the 3D box constructions.



Figure 4.2 Illustration of cell transformation. The original unit cell is shown in the blue parallelogram. The new pseudo-orthorhombic cell is highlighted in the bold red rectangle. Structure model 1 is an example of a tilted prolate constructed using the original cell and model 2 is a perfect prolate obtained from the transformed unit cell.

The unit cell transformation is given by the following matrix:

$$G = \begin{pmatrix} 2 & 0 & 1\\ 0 & 1 & 0\\ 0 & 0 & 1 \end{pmatrix}$$
(124)

A recent FTIR measurement on the  $TiO_2$ -B nanoparticles showed the presence of surface hydroxyl groups<sup>127</sup> which presumably resulted from sample preparation and/or moisture contamination. However, due to the low scattering power of H atoms, these hydroxyl H atoms were neither considered in the modelling nor in further data simulation. In addition, the different environments of O and Ti atoms on or close to the surface might result in a deviation of the surface structure from the average in the bulk. Nevertheless, to attain a structure that models the average local structure and the morphology of the particles, the surface contribution, such as surface relaxation, is not included in this study.

# 4.4 **Results and Discussion**

#### 4.4.1 Laboratory XRPD and TEM



Figure 4.3 Laboratory XRPD pattern of  $TiO_2$ -B nanoparticles (black circles), in comparison with the calculated pattern with no size effect considered (red lines). The main reflections are indexed in blue. The 020 reflection is marked with a red arrow.

The calculated XRPD pattern with no size effect shows multiple reflections (red pattern in Figure 4.3) due to the low space-group symmetry of the Bronze phase (C2/m). This is the pattern that would be observed from large crystals. However, the experimental XRPD shows a significant broadening. A Debye refinement study on the same nanoparticles revealed little evident strains<sup>127</sup>, indicating the peak broadening is mainly a result of a reduced particle size. The increased peak width leads to extensive peak overlap, which consequently makes the

study of anisotropic shape of the nanoparticles using the relative intensity of the individual Bragg reflection challenging.

Nonetheless, a careful examination of peak widths revealed that most broad peaks are composed of multiple overlapping reflections. This is not the case for the peak at about  $48 \,^{\circ}2\theta$  which arises almost completely from the 020 reflection. The observation that this reflection is ever broader than most other reflection suggests the particle probably has a smaller dimension along the [0k0] direction, which is the *b*-axis.



Figure 4.4 TEM image of the TiO<sub>2</sub>-B nanoparticles, adapted from the article published by Ren *et al.* in  $2012^{35}$ . Primary particles indentified in the prior study are highlighted with the white rectangular boxes; particles with more spherical shapes are highlighted with red spheroids.

The TEM image (Figure 4.4) demonstrates a severe aggregation of the TiO<sub>2</sub>-B nanoparticles. It is very difficult to differentiate an individual particle among these agglomerates. In that case, the morphological study needs to be performed on a large sample size to obtain good statistics resulting in reliable size information. An evaluation of about 100 nanoparticles was previously performed by Ren et al.<sup>35</sup>, which gave rise to an average size of ca.  $2.5 \times 4.3$  nm (aspect ratio = 1.72). As illustrated within the white boxes in Figure 4.4, the particles have an elongated shape. In the edge region of the agglomerates where the particles are relatively more isolated, some particles with more spherical shapes can be identified (highlighted with red spheroids in Figure 4.4). The observation is vague. However, it suggests

that according the TEM image (Figure 4.4) acquired from that particular perspective and at that specific spot, there are particles possibly with shapes other than just elongated ones. A recent Debye refinement study on the same sample reported prolate-like particles which have an average size about 3 nm with aspect ratio of C/A = 1.79 and aspect ratio of  $C/B = 1.72^{127}$ . This is consistent with the aspect ratio value reported in the TEM study.

#### 4.4.2 Small-angle X-ray Scattering

On the basis of the reported dimension obtained from the TEM data<sup>3</sup> and Debye refinement<sup>8</sup>, the SAXS analysis was first attempted using the prolate model. The best fit (Figure 4.5a) indicated that the mean average radius is about 1.5 nm with a full width at half maximum (FWHM) of 1.2 nm for the distribution (Figure 4.5b). The aspect ratio was optimized to 1.87 from the initial value of 1.72.



Figure 4.5 Experimental SAXS data (black circles) for  $TiO_2$ -B nanoparticles with the fits using prolate (blue dash) and oblate (red solid) models, and the corresponding size distributions (b).

As demonstrated in Figure 2.11, the shape functions from prolate and oblate spheroids that have similar volumes show similar profiles. Therefore the analysis was also performed using an oblate model. The simulated pattern shows few differences to the one from the prolate (Figure 4.5a). This observation suggests that both prolate and oblate models can be used to describe the shape of the particles according to the SAXS fitting. Specifically, the oblate that models the sample has an aspect ratio of 0.68 and a mean radius of 2 nm, with a

particle size distribution of 1.8 nm, slightly larger than that for the prolate case. The optimized parameters are listed in Table 4.1 for both the prolate and oblate model. The volume-weighted distributions of mean radius for both models imply that the sizes of the nanoparticles are non-uniform.

Table 4.1	Results	from	the	SAXS	analysis
-----------	---------	------	-----	------	----------

	prolate	oblate
Aspect Ratio	1.87	0.68
Schulz-Zimm Mean / Å	14.9	20.2
Schulz-Zimm Width / Å	12.4	18.2

### 4.4.3 Spherical Model

### 4.4.3.1 Real-space Least-squares Refinement



Figure 4.6 Experimental PDF (black circles), refinement (calculation: red, difference: orange in the bottom) and the simulations (blue and green) for TiO<sub>2</sub>-B nanoparticles. Sign "Ø" (diameter) marks the signal termination of the experimental PDF at about 32 Å. Refinement suggests a particle size of 3.2 nm. Simulations were performed using spherical particles with diameters of 3.6 nm (blue) and 2.8 nm (green).

The first peak at 1.92 Å corresponds to the average Ti-O bond length in the first coordination shell of the Ti atoms. The second peak at 3.08 Å refers to the nearest Ti-Ti atom pairs. The third peak comprises both Ti-O and Ti-Ti atom pairs. A detailed breakdown of the contribution from different atom pairs in the r-range of 0 - 10 Å is shown in Figure 4.7. It is

worth noting that there is a small shoulder in the first peak at about 2.1 Å, which arises from the elongated Ti-O bonds in the distorted TiO<sub>6</sub> octahedra in the structure. The PDF correlations are barely visible above the noise approximately at 32 Å (marked by Ø in Figure 4.6) indicating an average particle size of about 3.2 nm. This is consistent with the value obtained from the qualitative analysis of the TEM data<sup>35</sup>.



Figure 4.7 PDF contributions from Ti-O (red), Ti-Ti (blue) and O-O (green) atom pairs, in comparison with the experimental pattern (black circles). The calculations were performed from the refined structure using PDFgui.

The real-space least-squares refinement was performed against the experimental PDF in the r-range of 1.55 - 40 Å, using the reported structure<sup>130</sup> (Table 4.2) of the bulk material. The structure refinement (employing spherical models), which refined the diameter of the particles, suggested a particle size of 3.2 nm, consistent with the aforementioned observation value from the signal termination of the PDF. The difference PDF between the experimental data and the calculation is shown in Figure 4.6. The refinement shows a good fit in the short-range, where the residual made up primarily of noise. However, for the r-distance larger than 20 Å, the difference PDF starts to resemble a real signal, indicating the mismatch contains real morphological and structural information.

### 4.4.3.2 PDF and XRPD Simulation

To explore how the size effect might lead to the discrepancy between the experimental and calculated PDF in the refinement, two spherical  $TiO_2$ -B particles with one shorter (2.8 nm) and the other longer (3.6 nm) diameters were constructed, and the corresponding PDFs were simulated and compared to the experimental PDF (Figure 4.6). The 2.8 nm particle showed an even larger mismatch in the long range, as compared to that in the 3.2 nm refinement result. Although the 3.6 nm particle gave an excellent fit in the long range, the peaks in the intermediate range from 10 - 20 Å all have higher intensities. These comparisons

demonstrated that the mismatches in the refinement cannot be reduced by varying the particle size of the sphere model.

As mentioned previously in Section 2.1.7.5, only the sphere model is implemented in the PDFgui software, which in practice is applied in all data refinements of nanoparticles regardless of the actual shapes. Our SAXS analysis revealed the aspect ratio of the ellipsoid (1.87 for prolate and 0.68 for oblate) has a large deviation from the perfect sphere (aspect ratio = 1.0). Comparing the shape functions of sphere with a radius of 1.5 nm ( $\emptyset$  = 3.0 nm) and ellipsoid models with the same volume (Figure 2.11), the differences in the PDF start to be noticeable at around 10 Å. The differences become more pronounced at longer ranges, where the refinement shows the most significant mismatches with experiment, as reflected by the difference PDF (Figure 4.6). Hence, the discrepancy between the experimental PDF and the calculated pattern using the sphere model can be mainly attributed to an inappropriate particle shape function employed in the course of the structure refinement<sup>126</sup>.



Figure 4.8 Lab XRPD (black circles) compared with the simulations using spherical particles with sizes which range from 3.6 (blue), 3.2 (red) and 2.8 (green) nm. The intensity reduction from the 3.6 nm to the 2.8 nm model is a reflection of the fewer atoms in the structure due to the smaller size of the particle.

Simulations of XRPD patterns were performed using a spherical model with sizes of 2.8, 3.2 and 3.6 nm that have been studied in the PDF analysis. Poor fits are observed in the comparison between the experiment and simulations, confirming a poor description of the particle shape by using spherical models. The extensive peak overlap due to the limited particle size of 2.8 nm results in much broader peaks compared to the experimental data, suggesting a larger size should be considered to model the actual particles. The 110 reflection

in the simulation from a 3.2 nm particle, a size indicated by the PDF refinement, shows a stronger intensity compared to the 002 reflection. However, the 001 reflection in the experimental pattern has a lower intensity in contrast to the 002 reflection. The simulation from the 3.6 nm model, exhibits the most resemblance to the experimental pattern, but shows an isotropic peak broadening like the other two models. Hence a spherical model fails to explain the origin of the noticeable broadening of the 020 reflection.

### 4.4.4 Prolate Model

### 4.4.4.1 Prolate Model Construction

In order to construct more complex models, it is important to attain a set of more precise lattice parameters and atomic positions. To this end, the PDF structure refinement was performed again, however, in a much smaller *r*-range (1.55 - 15.8 Å) than used in the first refinement. The upper limit of the *r*-range, 15.8 Å, was determined from the length of the diagonal across the body of the unit cell. Considering the PDFs in the short range comprise information of only the nearest neighbours, they are less influenced by the shape of the particles than the PDFs in larger *r*-distances. For comparison, the refined lattice parameters are listed together with the reported value for the bulk phase in Table 4.2.

parameters	literature (bulk) <sup>130</sup>	refinement (nanoparticle)		
<i>a</i> / Å	12.1787	12.18		
<i>b</i> / Å	3.7412	3.75		
<i>c</i> / Å	6.5249	6.48		
α;β;γ/°	90.0 ; 107.054 ; 90.0	90.00 ; 106.94 ; 90.00		
$V/\text{\AA}^3$	284.22	283.12		
$\rho$ / g cm <sup>-3</sup>	3.733	3.75		

Table 4.2 Reported and Refined Structural Parameters for TiO2-B

The aspect ratios of all the prolate models were set as 1.87 (Table 4.2), to accord with the previous SAXS analysis; the  $r_{major}$  and  $r_{minor}$  of the prolate spheroid were calculated by assuming the same volume as the sphere with a diameter of 3.2 nm, indicated by the PDF refinement. Given by these two parameters, a prolate structure, with a major radius of 2.4 nm and minor radius of 1.3 nm, can be determined. The final models elongated along *a*-, *b*-, and *c*-axes were constructed (see Section 4.3 for details about prolate structure modelling), and individually examined in the further analyses.



Figure 4.9 Illustrations of the prolate models (aspect ratio = 1.87;  $r_{major}$  = 2.4 nm;  $r_{minor}$  = 1.3 nm) created from the pseudo-orthorhombic cell transformed from the original monoclinic unit cell (Figure 4.2), with the major axis along (a) *a*-, (b) *b*- and (c) *c*-axes.



4.4.4.2 PDF and XRPD Simulation

Figure 4.10 Experimental (black circles) PDF in comparison with the simulations from the asconstructed prolate models and the sphere (blue) with a diameter of 3.2 nm. Letters 'a', 'b' and 'c' in legend refer to the corresponding elongated axis of each prolate model. For a clearer view, the y-scales of the PDFs in the range of 10 - 35 Å are magnified by a factor of 2.5 relative to those in the short range.

The simulated PDFs and XRPD patterns using the as-constructed prolate models are shown in Figure 4.10 and Figure 4.11 respectively.

As shown in Figure 4.10, the PDF simulations from various models all produced an excellent fit to the experimental pattern in *r*-distances smaller than 10 Å, suggesting that the short-range PDF does not either depend on the shape or the asymmetry of the particle. The discrepancy between the simulation and the experiment becomes discernible at distances larger than 10 Å. In addition, the intensity mismatch varies depending on the shape and asymmetry of the particle model that was used. Although a prolate structure elongated along the *c*-axis was proposed by the Debye refinement study<sup>127</sup>, a comparison of those simulated PDFs showed a poor fit with all three prolate models, indicating none of them can represent the actual nanoparticles.



Figure 4.11 Experimental (black circles) XRPD pattern and simulations using the structure models that were used in the PDF simulations (Figure 4.10). Patterns were shown in the same colour codes. Pattern from a crystal phase is shown in the bottom to assist in the Bragg peaks indexing. The short dashed lines indicate the peak positions of the experimental data, to allow an easy comparison of the apparent peak shifts in the simulated patterns.

The above conclusion could be further verified by examining their powder diffraction patterns. Compared to the experimental pattern, the peaks containing 001, 002 and 003 reflections, which are significantly overlapped with other reflections, show either a positive or negative apparent shift for "prolate a" and "prolate c" model, respectively. These apparent shifts are a result of the structure asymmetry of the models that varies the intensities of individual reflections. The simulation using "prolate b" model, however, delivered two sharp

peaks for both 110 and 020 reflections, which is contradictory to the experimental data. As discussed previously, the anisotropic broadening of the 020 reflection indicates a smaller dimension of the particle along the *b*-axis, therefore ruling out "prolate b" structure as a candidate model.

Interestingly, apart from "prolate a" and "prolate c" models having opposite apparent shifts of peak positions in the simulated XRPD patterns, they also show a complementary mismatch of the PDF intensity. Hence, a hybrid model using a mixture of "prolate a" and "prolate c" with different ratio was then studied. Surprisingly, the mixture with an exactly 1:1 ratio produced the best fits to both the PDF and XRPD experimental data. Because the SAXS analysis showed an equally good fit when an oblate model was used, and the XRPD pattern reflected a smaller dimension along the *b*-axis, an oblate structure contracted along the *b*-axis was considered.

### 4.4.5 Oblate Model



Figure 4.12 Oblate model with an aspect ratio = 0.68,  $r_{major} = 1.9$  nm and  $r_{minor} = 1.3$  nm, shown from four different view: (a) [111] direction, (b) projection onto the *bc*-plane, (c) projection onto the *ac*-plane, and (d) projection onto the *ab*-plane.

The SAXS analysis using the oblate shape yielded a model (Table 4.1) with an aspect ratio of 0.68 and a mean radius of 20 Å. Considering it is volume-weighted mean, and has a broader

size distribution than the prolate model (Figure 4.5), several oblate models with various major and minor radii were then constructed and studied. The  $r_{major}$  and  $r_{minor}$  were determined in a similar manner as the prolate model, which is to calculate the major and minor radii by constraining an aspect ratio of 0.68 and assuming that the oblate model has the same volume as a sphere with a radius of  $1.6 \pm 0.1$  nm (that is within a range of 1.5 - 1.7 nm). The sphere radius of 1.6 nm was taken from the PDF refinement.

Among those oblate models that were studied, the one with a  $r_{major}$  of 1.9 nm and a  $r_{minor}$  of 1.3 nm, as illustrated in Figure 4.12, showed the best fits to the experimental PDF and XRPD pattern (Figure 4.13). For the PDF data, the size distribution of particles was not included in the data simulation, therefore the slight intensity mismatch of the PDF in the intermediate range (Figure 4.13a) is possibly due to the variation of size (and possibly, aspect ratio) of the actual sample.



Figure 4.13 Experimental (black circles) PDF and XRPD pattern in comparison to the simulations (red) using the oblate particle shown in Figure 4.12.

The XRPD simulation (Figure 4.13b) demonstrated a striking resemblance to the experimental data, and is noticeably better than the simulations (Figure 4.11) from other models that were investigated previously. More importantly, there was no discernible mismatch of peak positions and relative intensities of each peak; the 002 reflection showed an anisotropic broadening. Based on the good agreement between the simulations of the oblate

particle and experimental data, and the comparison of the simulations between the oblate and other models, it can be confirmed that the morphology of the actual  $TiO_2$ -B nanoparticles is an oblate, contracted along the *b*-axis, instead of a prolate elongated along the *c*-axis<sup>127</sup>.

Calculation studies<sup>125, 131</sup> revealed the Li diffusion path is preferably along the channel direction, that is, *b*-axis. Among all the structure models that have been investigated, the oblate model benefits from a maximum number of channels per unit volume with the shortest channel length for Li diffusion, thus leading to an extraordinary cycling performance. We can further relate the morphological advantage of the nanoparticles to their superior rate capability in comparison to the nanotubes. Although the TiO<sub>2</sub>-B nanotubes have nanoscale wall thickness, they grow with a microscale length along the *b*-axis. Hence, the long Li diffusion path, in combination with a smaller number of channels per unit volume, results in a drastic reduction in capacity when the cycling rate is increased<sup>35</sup>.

# 4.5 Conclusions

TiO<sub>2</sub>-B has drawn growing interest in the LIB community due to its promising characteristics as an anode material. Its good electrochemical behavior is believed to be strongly correlated with the unique structure, which contains three distinct sites for Li and open-channels along the *b*-axis. Studies<sup>125, 132</sup> show that size and morphology of the  $TiO_2$ -B also have a great impact on the electrochemical performance. Among different architectures, nanoparticulate TiO<sub>2</sub>-B shows the best cycling performance. However, due to the nature of nanoparticles, traditional crystallographic and microscopic methods are no longer sufficient to provide conclusive and accurate morphological and structural information. A recent TEM study<sup>35</sup> and XRPD analysis<sup>127</sup> via the Debye formula suggested the nanoparticles adopt an ellipsoid structure elongated along the *c*-axis. In this study, various models including sphere, prolate and oblate ellipsoids were constructed, based on the parameters obtained by SAXS fitting and PDF refinement. The asymmetry of the models due to the low symmetry of the monoclinic unit cell was also considered. XRPD and PDF patterns were simulated using these resulting structure models and compared to the experiment data, to attain a model that has the best description of the structure in both short and long range. The final comparison revealed that the nanoparticles have an oblate shape, contracted along the *b*-axis, instead of a prolate structure elongated along the *c*-direction, as previously reported by the Debye refinement study.

# 5 Study of the CuF<sub>2</sub> Conversion Mechanism

# 5.1 Introduction

To search for novel electrode materials that functions via new routes, many efforts have been recently devoted to binary metal oxides and fluorides, which operate via a conversion mechanism (Section 1.3.3) forming metal and Li<sub>2</sub>O or LiF phases during discharge, and returning to the original oxides or fluorides phase upon charging (Equation 3).<sup>36</sup>

# 5.1.1 Application of CuF<sub>2</sub> in LIBs

Depending on the oxidation state of the metal ion, Li incorporation involves more than one electron transfer, which leads to much higher capacities than observed for conventional insertion compounds such as LiCoO<sub>2</sub> and LiFePO<sub>4</sub>.<sup>36</sup> To search for new cathode materials, 3*d* transition-metal fluorides (MF<sub>x</sub>) have attracted considerable attention due to their ability to deliver high electrochemical energy density arising from the high free energy of formation of fluorides (see calculation in Section 1.3.3.1).<sup>37</sup> Among these 3*d* transition-metal fluorides, CuF<sub>2</sub> stands out as a promising candidate for the reason that it has a high specific capacity and the highest theoretical potential among all the divalent-3*d* transition-metal fluorides (see Table 1.2). These lead to an exceptionally high specific energy of 1874 Wh/kg (c.f. 600 Wh/kg for LiCoO<sub>2</sub>, shown in Table 1.1).<sup>37,40</sup>

$$CuF_2 + 2Li \xrightarrow[charge]{discharge}{2LiF} + Cu$$
(125)



Figure 5.1 Diagram of  $\text{CuF}_2$  conversion reaction (Equation 125), which shows drastic structural changes upon (re)conversion. The structure on the left corresponds to  $\text{CuF}_2$  ( $P2_1/n$ , distorted rutile), where Cu (blue) occupies the distorted octahedral sites. Structure on the top right is LiF (rock salt), where each Li (green) is 6-coordinated by F (orange) atoms. Cu model (face-centered cubic, fcc) is on the right bottom.

However, the electrochemical behavior of  $CuF_2$  is considerably different in practice. Its high sensitivity to moisture results in the presence of hydrated impurities in the anhydrous  $CuF_2$  and are responsible for significantly reducing the theoretical energy density, since their operating potentials are around 2 V instead of 3 V.<sup>41</sup> The large band gap due to the high electronegativity of fluorine makes  $CuF_2$  a poor electronic conductor. To enhance the conductivity, a mixed conductive matrix (MCM) approach has been developed, in which carbon or other compounds with excellent electronic and ionic conductivity such as MoO<sub>3</sub>, etc, are employed to improve electronic wiring.<sup>41</sup> Using this approach, a full theoretical capacity of  $CuF_2$  and an increased operating potential to 3 V can be reached. The enhanced electrochemical performance is believed to be derived from a combination of nanosizing the particles and connecting each domain with a conductive matrix, which enlarges the interfacial area for Li incorporation and shortens the tunneling length for electron transport.<sup>133</sup>

#### 5.1.2 Motivation of the Study

In comparison to the progress that has been made on discharge, however, good capacity retention after the first discharge has not been achieved. The mechanism underlying the electrochemical performance of conversion materials has been investigated for a variety of oxides and fluorides, and has emphasized the significance of electronic and ionic transport, volume expansion, and SEI formation, in modulating the discharge/charge cycling performance.<sup>134,133,135,136,137</sup> However, the insight from these studies cannot be straightforwardly applied to  $CuF_2$ , owing to its distinct electrochemistry, and both the sources of its irreversibility and the increasing overpotential after insertion of approximately one Li<sup>+</sup> per formula unit upon discharge<sup>41,133</sup> still remain unclear.

In this chapter, we investigated the  $CuF_2$  lithiation mechanism over a full cycle, aiming to gain a fundamental understanding of the whole electrochemical reaction. In particular, we elucidate the main factors that reduce the reversibility of this system. Due to its nano-structured nature, and the extensive chemical heterogeneity of the reaction, the pathway to acquire such knowledge is challenging. A variety of phase and structural characterization techniques to extract both short-range and long-range order are therefore required. Electrochemical tests including galvonostatic and CV experiments are first employed to obtain a comprehensive picture of the redox reactions in different potential windows. Structural and phase information concerning copper containing components are then obtained via *in situ* XANES and *in situ* PDF analyses. *Ex situ* solid state NMR is performed to investigate Li components present upon cycling. We demonstrate that NMR is a powerful approach to study phases containing either low X-ray scatterers, such as LiF, or low concentration solid-electrolyte interface (SEI) products.

# 5.2 Experimental

# 5.2.1 Materials Preparation

Carbon-coated nano-CuF<sub>2</sub> (CCN-CuF<sub>2</sub>) was prepared by ball milling commercial CuF<sub>2</sub> (Sigma-Aldrich 98%) and carbon black (Ketjen Black International Company). Two ballmilling methods were employed, planetary ball milling (PBM) (Retsch PM 100) and highenergy ball milling (HBM) (SPEX 8000M). Either 0.5 g or 1 g of a mixture composed of CuF<sub>2</sub> and carbon black (80:20 wt%) was prepared and placed into a milling jar in an Ar-filled glovebox. The jar was sealed with Parafilm before being transferred to the ball mill. For the PBM, a stainless steel jar (Rotec) with zirconia beads of various volume percentages (40 vol% and 70 vol%) was used. The milling process was programmed for various time periods at different speeds (300 rpm, 500 rpm and 600 rpm). For the HBM, a zirconia container with two zirconia balls was used and the milling was programmed for 45, 60 and 90 min.

# 5.2.2 X-ray Powder Diffraction

XRPD was performed on a laboratory Rigaku powder X-ray diffractometer with Cr K $\alpha$  (Cr K $\alpha$ :  $\lambda = 2.29$  Å) as a radiation source at a 0.12 %min scan rate from 2 $\theta$  range of 10 ° to 120 °. Samples were prepared in an Ar- or N<sub>2</sub>-filled glovebox. The powder samples were covered by Kapton films and sealed with vacuum grease (Dow) to minimize the exposure to moisture. LaB<sub>6</sub> was used as an external standard reference to obtain the instrumental broadening and to remove the systematic error caused by specimen displacement or zero shifts. Particle size analysis was performed using the Scherrer formula (see Section 2.1.6.5),<sup>67</sup> peak broadening being quantified via the integral breadth (IB) method,<sup>69</sup> *i.e.*, by using the ratio of the peak area to the peak height of the different CuF<sub>2</sub> reflections. Reflections with intensities less than 10% of the maximum were neglected in this analysis. The instrumental broadening was evaluated from the integral breadths obtained from the profile fitting of the first six reflections of the LaB<sub>6</sub> standard using second-order polynomials, while the strain broadening effects were neglected.<sup>138</sup> Lorentzian line-shapes were used in the profile fitting for all the reflections.

# 5.2.3 Electrochemical Characterization

The electrochemical properties of CCN-CuF<sub>2</sub> were evaluated with 2032 type coin cells and Swagelok cells. The cathode materials were prepared by mixing 85 wt% CCN-CuF<sub>2</sub> (HBM of 0.5 g for 60min) and 15 wt% carbon black (Super P). The cathode films were prepared by mixing 80 wt% CCN-CuF<sub>2</sub>, 15 wt% Super P and 5 wt% polyvinylidenefluoride (PVDF) as a binder in N-methylpyrrolidinone (NMP). The slurry was dispersed on either an aluminum or copper foil (Goodfellow) in air followed by drying in an oven at 80 °C. Two additional batteries, with one using only Cu foil as a cathode and the other a carbon mixture (50 wt% Super P and 50 wt% Ketjen Black) directly deposited on the stainless steel current collector, were also tested for comparison purposes. Both coin cells and Swagelok cells were assembled in an Ar-filled glove box with Li metal foil as anode. The electrolyte consisted of 1 M LiPF<sub>6</sub> dissolved in a mixture solution of ethylene carbonate (EC) and dimethyl carbonate (DMC) with a volume ratio of 1:1, except for one CV experiment in which ethyl methyl carbonate (EMC) was used as a solvent. Either Celgard or glass fiber (Whatman) was used as a separator. The galvanostatic cycling measurements were performed either in various potential windows or a specific capacity window at room temperature using Arbin battery cycling systems. The Li content in each sample was calculated from the theoretical discharge capacity of  $CuF_2$  (Li = 2.0 for 528 mAh/g), assuming 100% coulombic efficiency. Different cycling rates of C/n (n = 35, 50 and 100) were also investigated, where C stands for theoretical specific (dis)charge capacity (mAh/g) and n represents number of hours to reach the theoretical capacity. For all the *ex situ* studies, the samples were obtained from powder-based coin cells. When the cells reached the desired Li content or potential, the cells were stopped and dissembled in the glove box. The cathode powder materials were collected in a vial and rinsed by DMC to remove residual  $LiPF_6$  from the electrolyte. After drying overnight in a glove box, the washed cathode samples were stored in a glass container under inert Ar atmosphere until further measurement. Galvanostatic intermittent titration (GITT) experiments were performed on a Swagelok cell under a C/20 rate with a 3-hr current step and a 48-hr relaxation period. CV measurements were performed on coin cells in potential windows of 4.5 V - 2.0 V, 4.5 V - 1.3 V, 4.5 V - 0.4 V, and 4.5 V - 0 V vs. lithium metal with a scan rate of 0.1 mV/s.

# 5.2.4 X-ray Absorption Spectroscopy

The XANES spectra were collected at beamline X19A at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. The measurements were performed in transmission mode using a Si (111) double-crystal monochromator, which was detuned by 30% to minimize the presence of higher harmonics in the beam. Energy calibration was carried out by using the first inflection point in the spectra of Cu metal foil as reference (Cu K-edge: 8979 eV). A series of reference materials containing Cu atoms with different oxidation states were measured, which include CuCl, CuCl<sub>2</sub>, Cu<sub>2</sub>S, Cu<sub>2</sub>O, CuO, and CuF<sub>2</sub>.

The *in situ* cells were prepared using Al plates with Mylar windows.<sup>139</sup> Each cell was composed of a self-standing CCN-CuF<sub>2</sub> film (mass ratio of CCN-CuF<sub>2</sub>:Super P:polytetrafluoroethylene (PTFE) = 8:1:1) attached to an Al foil as current collector, a Li metal negative electrode with Cu mesh as current collector, a Celgard separator, and 1 M LiPF<sub>6</sub> in EC/DMC (volume ratio 1:1) as electrolyte. The *in situ* cell was fully discharged and then charged to a capacity corresponding to a Li content of approximately 1.5 per CuF<sub>2</sub> formula unit using a C/40 rate. A second, essentially identical, battery was then used to collect the data for the rest of the charge; a faster rate of C/17.5 and a cutoff potential of 4.1 V was used due to the limited beam time availability. The *ex situ* samples were prepared using coin cells cycled at C/100. Powder extracted from the dry electrode was then rubbed onto Kapton tape. The data was analysed using IFEFFIT and Demeter package.<sup>140</sup>

### 5.2.5 PDF from X-ray Total Scattering

X-ray PDF analyses were performed in situ and ex situ at beamline 11-ID-B at the Advanced Photon Source (APS) at Argonne National Laboratory. The total scattering data were collected at room temperature using an amorphous Si-based 2D detector with an X-ray energy of 58 keV (wavelength  $\lambda = 0.2127$  Å). For the *in situ* experiment, electrode pellets of CCN-CuF<sub>2</sub> which contained 20 wt% of carbon and 20 wt% of PTFE, were prepared and assembled into the AMPIX cell,<sup>141</sup> with a glass fiber as separator, a Li metal foil as counter electrode, and 1 M LiPF<sub>6</sub> in EC/DMC (volume ratio 3:7) solution (Tomiyama Pure Chemical Industries) as electrolyte.<sup>142</sup> The cell was cycled under a rate of C/20 at room temperature. The ex situ experiments were performed on fine powder samples which were sealed in Kapton capillaries filled under Ar atmosphere. The total scattering experiments were conducted in transmission geometry. A CeO<sub>2</sub> standard was used to calibrate the sample-to-detector distance and the tilt of the detector relative to the beam path. Scattering measurements for the empty Kapton capillary, as well as a reference AMPIX cell containing all the components in the same mass ratio except the active material, were also performed under the same experimental conditions to obtain the instrumental background.<sup>77</sup> Scattering data reduction, correction, normalization and PDF extraction were performed in the same manner as previously described in Section

3.2.3. A  $Q_{\text{max}}$  of 24.0 Å<sup>-1</sup> was used for *ex situ* experiments. *In situ* data were limited to a lower  $Q_{\text{max}}$  of 19.0 Å<sup>-1</sup> as the maximum accessible scattering angle was limited by the scattering aperture in the AMPIX cell.<sup>143</sup> Structure refinement were performed using the PDFgui software.<sup>118</sup> Previously collected scattering data for the Ni standard were processed and refined to obtain the instrumental parameters.

### 5.2.6 Solid-State NMR Spectroscopy

<sup>7</sup>Li MAS (see Section 2.3.2.1 for details about magic angle spinning) NMR experiments were performed on cycled CCN-CuF<sub>2</sub> samples with a 1.8 mm MAS probe designed by Samoson and coworkers on a Chemagnetic CMX-200 (4.7 T) and a Varian Infinity-Plus-360 (8.47 T) spectrometer at a <sup>7</sup>Li Larmor frequency of 77.8 and 140.2 MHz, respectively. All spectra were acquired at a spinning frequency of 38 kHz with a rotor synchronized echo sequence (see Section 2.3.2.2 for details about spin echo):  $\pi/2 - \tau - \pi - \tau - \text{acq}$ ; where  $\pi/2$  and  $\pi$  represent the 90° and 180° radiofrequency (RF) pulses, and  $\tau$  and acq stand for echo time and acquisition time periods, respectively. The spectra were referenced to a standard 1 M <sup>7</sup>LiCl aqueous solution at 0 ppm. A  $\pi/2$  pulse of 2.3 µs with a relaxation delay of 1.0 s was used on the CMX-200 spectrometer and a  $\pi/2$  pulse of 2.5 µs with a relaxation delay of 1.0 s was used on the Varian Infinity-Plus-360 spectrometer.

<sup>19</sup>F MAS NMR experiments on cycled CCN-CuF<sub>2</sub> samples were performed with a Chemagnetic 3.2 mm and the 1.8 mm probe (Samoson) on the Varian Infinity-Plus-360 spectrometer at a <sup>19</sup>F Larmor frequency of 338.73 MHz, with a spinning frequency of 20 kHz and 38 kHz, respectively. An echo sequence was used with a  $\pi/2$  pulse of 2.0 µs on both probes. A relaxation delay of 0.2 s was used on the 3.2 mm probe and 0.5 s on the 1.8 mm probe. All spectra were referenced to a standard CFCl<sub>3</sub> at 0 ppm. <sup>19</sup>F MAS NMR experiments on commercial CuF<sub>2</sub> and HBM CCN-CuF<sub>2</sub> were performed using a 1.9 mm Buker double resonance probe on Bruker AVANCEIII 200 MHz (4.7 T) spectrometer at a <sup>19</sup>F Larmor frequency of 188.3 MHz. A spinning frequency of 40 kHz was used with a  $\pi/2$  pulse of 2.3 µs and a 2.0 s relaxation delay. Spectra were referenced to the external standard LiF at -204 ppm.

SR experiments (see Section 2.3.2.4 for details) were performed on cycled CCN-CuF<sub>2</sub> samples with the 1.8 mm probe on the Varian Infinity-Plus-360 spectrometer to measure <sup>7</sup>Li and <sup>19</sup>F spin-lattice ( $T_1$ ) relaxation times. Saturation recovery times were arrayed from 10  $\mu$ s to 1 s for each measurement. Plots of integrated signal intensity versus saturation recovery time were fit to the equation y = amp(1-e<sup> $\tau/T_1$ </sup>) (Equation 123) using Chemagnetics Spinsight

software, where y is the integrated signal intensity, amp is the amplitude constant,  $\tau$  is the saturation recovery time, and T<sub>1</sub> is the spin-lattice relaxation time.

The <sup>31</sup>P MAS NMR experiment was performed on a fully discharged sample (Li = 2.0) with a Bruker 2.5 mm double resonance probe on Bruker AVANCEI 400 MHz (9.4 T) spectrometer at a <sup>31</sup>P Larmor frequency of 81.0 MHz. An echo sequence with a spinning frequency of 30 kHz was used with a  $\pi/2$  pulse of 2.5 µs and a relaxation delay of 5 s. The chemical shift was referenced to NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> at 0.81 ppm as a secondary reference.

<sup>19</sup>F → <sup>13</sup>C CP-MAS NMR experiments (see Section 2.3.2.3 for details about cross polarisation) were performed on the pristine CCN-CuF<sub>2</sub> sample using a Bruker 3.2 mm triple resonance probe on a Bruker AVANCEIII 700 MHz (16.5T) spectrometer. The <sup>19</sup>F → <sup>13</sup>C CP conditions were optimized on PTFE and then applied to the CCN-CuF<sub>2</sub> sample spinning at 20 kHz with a relaxation delay of 2 s and a CP contact time of 500 µs. <sup>19</sup>F continuous wave decoupling was applied during the <sup>13</sup>C signal acquisition at an RF nutation frequency of 70 kHz.

All spectra shown in the plots are normalized with respect to the sample weight, number of scans and receiver gain.

# 5.3 Results and Discussion

# 5.3.1 X-ray Powder Diffraction

Laboratory X-ray diffraction was performed on CCN-CuF<sub>2</sub> to investigate the size reduction effect induced by the different milling methods (PBM and HBM) and milling parameters (Table 5.1and Figure 5.2).

Material Preparation -		<b>Electrode Fabrication</b>	
		Film	Powder
	3 hr 500 rpm with 70 vol% ZrO <sub>2</sub> beads	$\checkmark$	$\checkmark$
PBM	36 hr 300 rpm with 40 vol% ZrO <sub>2</sub> beads	$\checkmark$	$\checkmark$
	24 hr 600 rpm with 40 vol% ZrO <sub>2</sub> beads	$\checkmark$	$\checkmark$
HBM	1 hr 1.0 g	×	$\checkmark$
	1 hr 0.5 g	×	
	1.5 hr 0.5 g	×	$\checkmark$

Table 5.1 Material preparation and electrode fabrication methods

An XRPD pattern for the commercial monoclinic  $\text{CuF}_2$  phase  $(P2_1/n)$  is given for comparison, and an analysis of the patterns shows that this phase is dominant in all the samples. The HBM method leads to significant peak broadening in all the CuF<sub>2</sub> patterns. However, no discernible difference with respect to the peak width was found for the different milling times. In comparison, the reflections in the patterns for the PBM samples showed either less (24 hr 600 rpm, 40 vol% ZrO<sub>2</sub> beads) or very little broadening (36 hr 300 rpm, 40 vol% ZrO<sub>2</sub> beads and 3 hr 500 rpm 70 vol% ZrO<sub>2</sub> beads) compared to commercial CuF<sub>2</sub>, even though a high milling rate and a long duration of milling time was used. Assuming that strain broadening gives a negligible contribution to the peak width, these observations suggested that HBM is a more effective approach compared to PBM in reducing the particle size of CuF<sub>2</sub>.



Figure 5.2 Laboratory XRD patterns for commercial  $CuF_2$  and  $CCN-CuF_2$  nanocomposites prepared under various conditions. The two main  $CuF_2$  reflections, (011) and (101), are labelled. The two reflections marked with asterisks at low angles correspond to impurity phases. The reflection at 18.8 ° 20 is assigned to Cu(OH)F and/or CuF\_2·2H\_2O. (HBM: high-energy ball mill, PBM: planetary ball mill)

The Scherrer formula<sup>67</sup> was employed to calculate the average particle size for the "HBM 1hr 0.5g" sample, giving an average particle size of about 10 nm. However, the observation of an extra Bragg reflection at  $17.6 \circ 2\theta$  and some very weak features between  $17 \circ - 27 \circ 2\theta$  in all the samples suggest the presence of impurities. The broad peak at about  $18.8 \circ 2\theta$  seen after ball milling is assigned to either the hydrated phase Cu(OH)F (main reflection at  $18.9 \circ 2\theta$ ) and/or CuF<sub>2</sub> 2H<sub>2</sub>O (main reflection at  $18.4 \circ 2\theta$ ). The intensity of this reflection was less pronounced in the HBM samples probably because the much shorter milling time leads to less moisture contamination.

### 5.3.2 Electrochemical Characterization

The electrochemical performances of both film- and powder-based cathodes containing the CCN-CuF<sub>2</sub> obtained with various milling parameters were investigated by galvanostatic cycling to select the optimal material preparation and electrode fabrication method (see Table 5.1). All the film-based batteries show a plateau at a potential of around 2 V in the first discharge profile (Figure 5.3), lower than that for the powder-based batteries. This is ascribed to the formation of a hydrated CuF<sub>2</sub> phase during film fabrication.<sup>41</sup> Thus the powder-based electrodes were employed for further investigation. Comparing the CCN-CuF<sub>2</sub> powderelectrodes obtained via PBM and HBM methods, the PBM CCN-CuF<sub>2</sub> powder-electrode exhibits a shorter plateau with a lower potential at around 2.8 V – 2.9 V. After reaction with ~ 0.3 mol of Li, the operating potential gradually slopes down, suggestive of an increase in overpotential. In contrast, following a pre-plateau feature A, the potential plateau for the HBM CCN-CuF<sub>2</sub> powder-electrode remains at 3.0 V (B) for up to 1 Li insertion. (The same labels A - D are used to mark the same processes in all electrochemistry figures, and the assignments of the various processes  $(A - E, B_1' - E')$  are summarized in Table 5.2). A sloping voltage is seen after 1 mol of Li incorporation. The significant difference in the electrochemical performance between the PBM and HBM powder samples can be ascribed to the smaller particle size and the fewer hydrated impurities present in HBM CCN-CuF<sub>2</sub>, which both appear to lead to a smaller polarisation overpotential. There are two distinct processes at around 2.5 V (B<sub>H</sub>) and 1.8 V (C) in the sloping region of the HBM electrode potential profile. Full capacity is reached at about 1.5 V. These potential profiles are similar to those reported in literature previously<sup>41,133</sup> and thus, the following studies are performed on the samples prepared by the HBM method. Because no discernible difference in electrochemistry was seen for the different HBM methods, a 0.5 g weight loading of composite and a 1 hour ball-milling duration were used in all subsequent studies.



Figure 5.3 Representative potential profiles for CCN-CuF<sub>2</sub> electrodes produced using different material preparation and electrode fabrication methods. Solid (Bold black: 1st cycle; Red: 2nd cycle; Blue: 3rd cycle), dash and dash-dot profiles correspond to the potential profiles for the HBM powder-based battery, the PBM powder-based battery, and the PBM film-based battery, respectively. All batteries were cycled with a rate of C/100. The same labels A – D are used to mark the same processes in all subsequent electrochemistry figures. The assignments of the labels are listed in Table 5.2.

The 1st charge curve for the sample HBM CCN-CuF<sub>2</sub> shows a specific charge capacity of 316 mAh/g, which is equivalent to 1.2 mol Li content per formula unit. The charge process starts with a steep rise in potential until it reaches a pre-plateau slightly above 3 V (C'). This is followed by a flatter region between 3.5 V and 3.8 V (B<sub>1</sub>' and B<sub>2</sub>'), and then the potential rises again until the upper limit used here of 4.5 V (D), leading to a large potential hysteresis in the first cycle. The specific capacities of the subsequent discharge cycles are reduced significantly and no plateaus are present in any of the subsequent discharge steps. Only about 32% and 16% of the specific capacity were obtained in the 2nd and 3rd discharge process, respectively. After the 3rd cycle, the specific capacity of the HBM CCN-CuF<sub>2</sub> cathode is negligible.



Figure 5.4 GITT for the first cycle of the CCN-CuF<sub>2</sub> electrode, under a C/20 rate with a 3-hour current step and a 48-hour relaxation period.

The GITT curve for the first cycle is shown in Figure 5.4. The equilibrium potential after relaxation at the beginning of discharge and at the end of charge is almost identical. During the 1st discharge, before 1.2 mol of Li reaction, a constant equilibrium potential is observed at ca. 3.25 V, indicative of a two-phase reaction. When the intermittent discharge is continued beyond approximately 1.2 Li, a drop of the equilibrium potential is observed suggesting that additional processes are occurring. Upon charge, the equilibrium potential reaches the upper limit of 4.5 V.

In order to study the electrochemical processes taking place upon cycling in further detail, CV measurements were performed for different potential windows of 4.5 V – 2.0 V, 4.5 V – 1.3 V and 4.5 V – 0.4 V vs. lithium metal (Figure 5.5). Figure 5.6 shows the electrochemical profile for the CCN-CuF<sub>2</sub> cathode discharged to 0 V in caparison with the potential curves for a Cu foil and carbon mixture cathodes.



Figure 5.5 First sweeps in the cyclic voltammograms of a CCN-CuF<sub>2</sub> electrode for different potential windows (Red: 4.5 V - 2.0 V; Blue: 4.5 V - 1.3 V; Black: 4.5 V - 0.4 V) with a scan rate of 0.1 mV/s. The current is normalized per gram of active material.



Figure 5.6 Potential profiles for batteries using CCN-CuF<sub>2</sub> (black), Cu foil (blue) and carbon mixture (red) as cathode materials discharged to 0 V. The capacity from Cu foil has been scaled by  $10^3$  for a better comparison. The inset shows a dQ/dV plot converted from the potential profiles.

In Figure 5.5, all three curves exhibit a small reduction peak at around 3.3 V (A) and a large reduction peak at 2.6 V (B) in the cathodic sweep. The 3.3 V peak is tentatively ascribed to reactions with the possible impurities in HBM CCN-CuF<sub>2</sub>, and will be discussed in more

detail in the NMR section. The peak at 2.7 V corresponds to the lithiation of CuF<sub>2</sub> to form Cu metal. Comparing the redox pairs found in the potential window of 4.5 V - 1.3 V to those in the potential window of 4.5 V - 2.0 V, we make the following observations: (i) the small feature at around 1.7 V (C) is correlated to the extra oxidation peak at 3.2 V (C') and (ii) the anodic current for the oxidation peak at 3.58 V (B<sub>1</sub>') decreases following discharge to 1.3 V. With the cutoff potential lowered to 0.4 V, another intense reduction peak appears at about 0.65 V (D), corresponding to plateau D in Figure 5.6. On the anodic sweep, new features are observed: (i) a broad feature around 1.0 V (E'), (ii) the absence or significant reduction of the oxidation peak at 3.58 V (B<sub>1</sub>'), and (iii) an intense oxidation peak at 4.4 V (D'). The reduction processes at 1.7 V (C) and 0.65 V (D) are tentatively ascribed to the cathodic formation of SEI due to the reduction of electrolyte, while the oxidation peaks at 3.2 V (C') and 4.4 V (D') can be attributed to the oxidation of the SEI products formed during the C and D processes.<sup>144,145,146,147,148</sup> A recent CV study on the fluoride conversion material BiF<sub>3</sub> ascribed the reduction peaks at 1.7 V and 0.8 V to EC and DMC decomposition, respectively.<sup>149</sup> However, the reduction feature C is also present in our CV experiment on the 1 M LiPF<sub>6</sub>/EMC electrolyte (an EC free) system, which indicates that the reduction process C in our system is likely dominated by the linear carbonate DMC rather than cyclic carbonate EC. The dQ/dV plot obtained from the reference cathodes, copper foil and carbon (inset of Figure 5.6), reveals that peak C is only observed when Cu is present while peak D occurs when carbon is used, suggesting that the decomposition of the electrolyte on the surface of the cathode occurs at different potential values for different components of the cathode. We can thus attribute reaction C to the electrolyte decomposition, possibly dominated by DMC decomposition, on the copper surface, and D to EC/DMC decomposition on the carbon surface. The features E in the cathodic sweep, and E' in the forward anodic sweep, which are only present in the CV with a large potential window (4.5 V - 0.4 V or 4.5 V - 0.0 V), are also attributed to the electrolyte reactions related to carbon. <sup>150,151,152,153</sup>

In the CVs obtained with a potential window of 4.5 V - 2.0 V and 4.5 V - 0.0 V vs. lithium metal (Figure 5.7a and b), a large reduction of current response is observed after each sweep, reflecting capacity loss and poor cyclability of CCN-CuF<sub>2</sub> in both potential windows. In addition to the intensity reduction or the loss of peak B (the conversion reaction of CuF<sub>2</sub>), both peaks C and D show less pronounced intensities in the subsequent sweeps. This is ascribed to the passivation effect of the SEI layer, which provides kinetic stability to the electrolyte against further reduction upon successive scans, resulting in a smaller current.<sup>154</sup>



Figure 5.7 First three / four sweeps in the cyclic voltammograms of the CCN-CuF<sub>2</sub> in the potential window of (a)  $4.5 \text{ V} \sim 2.0 \text{ V}$  and (b)  $4.5 \text{ V} \sim 0.0 \text{ V}$  with a scan rate of 0.1 mV/s. The current is normalized per gram of active material and each label indicates a redox process defined in Table 5.2. (Black: 1st sweep; Red: 2nd sweep; Blue: 3rd sweep; Olive: 4th sweep)

# 5.3.3 XANES

Many detailed XANES analyses are performed based on the studies of well-characterized model compounds as references, and the characteristic near-edge structure for Cu(I) and Cu(II)

are often utilized for fingerprinting the valence state and their coordination environments.<sup>86</sup> To this end, a series of Cu containing reference compounds were first measured and their normalized XANES spectra along with their corresponding 1st derivatives are shown in Figure 2.15a and b, respectively; the first peak in the derivative indicating the K-edge position of each Cu species. The edge positions are located at 8979, 8980 – 8982 eV for Cu and Cu (I) species, respectively, while Cu(II) compounds all have even higher K-edge energies. Among the Cu(II) compounds, CuF<sub>2</sub> shows the highest edge energy of about 8988.8 eV, due to the larger electronegativity of F (and thus lower electron density nearby Cu<sup>2+</sup>) as compared to O and Cl.



Figure 5.8 First derivatives of the normalized Cu K-edge XANES spectra of commercial  $CuF_2$  (red dash) and HBM CCN-CuF<sub>2</sub> (black solid). The insert shows a magnification (×10) of the spectra in the same energy region. An additional absorption peak is present around 8980 eV in HBM CCN-CuF<sub>2</sub>, suggestive of the presence of Cu<sup>+</sup> components.

Figure 5.8 shows the 1st derivative of the Cu K-edge XANES spectra for HBM CCN-CuF<sub>2</sub> and commercial CuF<sub>2</sub>. A small peak corresponding to the pre-edge feature in the CuF<sub>2</sub> XANES spectrum is observed at 8976 eV, which is assigned to the 1*s*-3*d* electric-dipoleforbidden quadrupole-allowed transition.<sup>84,86</sup> The other two peaks at about 8989 and 8993 eV were attributed to the 1*s*-4 $p_z$  and 1*s*-4 $p_{x,y}$  dipole-allowed transitions, respectively, in an earlier polarisation-dependent XAS study.<sup>155</sup> A weak peak at about 8980 eV is observed in the 1st derivative spectrum for the HBM CCN-CuF<sub>2</sub> sample, but is absent in the commercial CuF<sub>2</sub> spectrum. On the basis of the analysis of the reference spectra, this peak can be ascribed to the presence of a Cu(I) species introduced by the ball-milling procedure. The Cu(I) impurity might arise from a reduction process caused by the presence of carbon at the elevated temperatures that are induced by the HBM process. This Cu(I) species is either present in sufficiently low quantities and/or is amorphous so that it could not be detected by XRPD. In addition, a positive shift of 0.4 eV in the edge-energy was found for HBM CCN-CuF<sub>2</sub> relative







Figure 5.9 (a), (b) The normalized Cu K-edge XANES spectra observed in situ on discharge and charge, respectively. The spectrum for Cu metal reference is included. Black arrows indicate the direction of evolution of Cu phase. The insets show the electrochemistry and the mole fractions of the CuF<sub>2</sub> component extracted from the LCA of the corresponding XANES spectra using the spectra of Cu metal and CuF<sub>2</sub> as references. For the LCA on charge, a three-standard fit using Cu(I)Cl as the third standard was also attempted, which is shown in Figure 5.13d. (c) The corresponding 1st derivatives of the normalized difference XANES spectra shown in (a). (d) Select 1st derivatives of the normalized difference XANES spectra and Li 2.0 on charge) from the subsequent spectra (shown in (a)) obtained on cycling, e.g., "Li 0.5 - Li 0" in (c) corresponds to a subtraction of spectrum Li 0 from Li 0.5 (a); the derivative plots show the change in the various components. Three spectra "Li 1.8 - Li 2.0", "Li 1.4 - Li 2.0" and "Li 0.8 - Li 2.0" have been highlighted in (d), so as to allow a more ready comparison with the 1st derivatives of the normalized XANES spectra of the reference spectra have been scaled with the coefficients shown in the brackets. Arrows indicate the direction of evolution of the 1st derivative peaks.

The normalized Cu K-edge XANES spectra for *in situ* discharge and charge, including the Cu metal reference, are shown in Figure 5.9a and b, respectively. The insets show the electrochemistry and the mole fraction of the CuF<sub>2</sub> component extracted from linear combination analysis (LCA) of the XANES spectra using the Cu metal and CuF<sub>2</sub> reference spectra. The corresponding 1st derivatives of the normalized difference XANES spectra are shown in Figure 5.9c and d. Upon discharge, the peak at around 8981 eV, which corresponds to the 1s-4p transition for Cu metal, was observed to grow, <sup>156</sup> consistent with the reduction of Cu(II)F<sub>2</sub> to Cu metal. The presence of an isosbestic point indicates a two-phase conversion reaction. Meanwhile the two main peaks identifying CuF<sub>2</sub> components grow in negative intensity (in the 1st derivative of difference XANES: Figure 5.9c) due to the reduction in phase fraction of CuF<sub>2</sub>. Note that the overlap of the 1st derivatives of Cu metal and CuF<sub>2</sub> in this energy range result in different line shape for the two 1st derivative peaks for CuF<sub>2</sub> in the composite as compared to the CuF<sub>2</sub> reference. Such alteration of the peak line shape from the superimposition of multiple spectra is also present in the 1st derivative difference spectra upon charge. No peaks between 8980 - 8982 eV corresponding to Cu(I) species were observed. These observations confirm that the discharge process involves a single-step conversion reaction that proceeds directly from CuF<sub>2</sub> to Cu without forming any intermediate Cu(I) species. On the basis of the mole fraction from the LCA (inset of Figure 5.9a), the conversion reaction starts to slow down at Li = 0.9, which coincides with the kink in the potential profile, indicating that side reactions are occurring in the sloping region. This is consistent with the GITT results, confirming that multiple reactions are taking place at this point. Consequently, about 8% of CuF<sub>2</sub> remains unreacted when the theoretical discharge capacity is reached.

The XANES spectra of HBM CCN-CuF<sub>2</sub> cathode upon charge shows a reduction in intensity of the Cu peak at about 8981 eV (Figure 5.9b) and an increase in negative intensity of the peak in the first derivative at 8979 eV (Figure 5.9d), indicating the loss of Cu metal. The positive peaks in the 1st derivative difference spectra are attributed to the formation of higher oxidation state Cu species. Among those peaks, the ones at 8982 and 8986 eV reach a maximum at Li =  $\sim 1.2 - 1.4$ . The peak at 8982 eV then starts to decrease while the peak at 8986 eV stops growing in intensity. However, the peaks at 8986 and 8993 eV maintain a steady growth until a capacity of Li = 0.8 is reached. All three Cu(I) reference compounds studied here (Figure 2.15) give rise to edge energies between 8980 – 8982 eV, and the line shape of the "Li 1.4 - Li 2.0" 1st derivative shows the closest resemblance to that of the CuCl

reference. According to the fingerprinting theory for Cu(I) species proposed by Kau et al.,<sup>86</sup> the peaks seen at 8982, 8986 and possibly 8993 eV for the "Li 1.4 - Li 2.0" spectrum can be assigned to a Cu(I) species with tetrahedral geometry, similar to that found in CuCl. Some possible assignments can be envisaged: (i) Cu(I)F instinctively comes to mind since the Cu<sup>+</sup> cation is formed in a F<sup>-</sup> rich system. However, as the only missing member in the cuprous halides family, CuF is not thermodynamically stable.<sup>157,158,159</sup> (ii) a structure containing Cu(I)F<sub>4</sub><sup>3-</sup> tetrahedra, and (iii) an oxygen containing Cu(I) species<sup>160</sup> with oxygen originating from the impurities in the composites and electrolyte. As charging proceeds, an intensity reduction of the 8982 eV peak and a growth of the 8986 and 8993 eV peaks are observed, which indicate a further oxidation of Cu or Cu(I) to a Cu(II) species where the Cu local environment is similar to that in the CuF<sub>2</sub> structure.



Figure 5.10 PCA is performed in the energy region of 8959 - 9059 eV on (a) XANES spectra of 1st charge and (b) the corresponding 1st derivatives. Only the first four components weighted by eigenvalues are shown. The first two components (1: black, and 2: red) clearly dominate both spectra. At least one more component (3: blue) appears to be above noise (4: green) in the edge region (~ 8980 - 8990 eV) where the changes between Cu, Cu(I) and Cu(II) are the greatest, suggesting the presence of a third phase<sup>161</sup>

Principal component analysis (PCA) (Figure 5.10) and target transformation (TT) (Figure 5.11) were performed on the XANES spectra obtained on charge and their 1st derivatives, to determine the number and nature of the distinct phases.<sup>161,162</sup> The results demonstrate that while the first two components dominate the spectra in the edge region (~ 8980 - 8990 eV), at least one more component appears above the noise in the energy range corresponding to Cu(I) and Cu(II). This is further confirmed by the comparison between the data reconstructions using two and three phases (Figure 5.12). These observations indicate the



presence of a third phase, which is difficult to identify. However, the TT results reveal that it contains Cu(I) in a local environment close to the tetrahedrally-coordinated Cu(I) in CuCl.

Figure 5.11 Goodness of fit (chi-square: black column; R-value: red column) of the TT using (a) 2 components and (b) 3 components obtained from the PCA analysis shown in Figure 5.10a. Of the library of the measured references, and in addition to Cu and  $CuF_2$ , CuCl has the lowest goodness of fit and is the best third standard for the LCA analysis in the case of three-phase coexistence.



Figure 5.12 Data reconstruction on XANES spectrum of Li = 1.5 using (a) 2 components and (b) 3 components. The misfit in the edge region (8980 - 8990 eV) is smaller in the residual for 3 components than that for 2 components, demonstrating the presence of one more distinct phase than two.

LCA was then performed with a three-component fit using Cu(I)Cl as the third standard (Figure 5.13d), and was compared to an LCA with a two components employing

only Cu(0) and Cu(II)F<sub>2</sub> as standards (Figure 5.13c). Both results show that a large decrease in the Cu(0) fraction and an increase in the Cu(II) fraction occur from Li =  $\sim 1.8 - 1.0$ , corresponding to the region around 3.6 V (B<sub>1</sub><sup>'</sup> and B<sub>2</sub><sup>'</sup>) in the galvanostatic curve; this is ascribed to the Cu(0)  $\rightarrow$  Cu(II) oxidation process. The evolution of the Cu(I) fraction is captured in the three-standards fit, which shows the formation of Cu(I) species from the beginning of charge till a capacity of around Li = 1.5; this is followed by a further oxidation to Cu(II).



Figure 5.13 Comparison of the goodness of fit: (a) chi-square and (b) R-value between the LCA using a 2-standard fit (black squares) and 3-standard fit (red dots); and the corresponding mole fractions between (c) 2 standards: Cu (red) and CuF<sub>2</sub> (blue) and (d) 3 standards: Cu (red), CuCl (green) and CuF<sub>2</sub> (blue). The LCA using a 3-standard fit clearly shows an improvement in R-values for Li contents of less than 1.7. The mole fractions presented in (c) are equivalent to the ones presented in the inset of Figure 5.9b.

### 5.3.4 X-ray PDF





Due to the limited domain size of nanomaterials, their structures are not easily studied by a conventional crystallographic approach using Bragg scattering. To investigate the phase transformation in an atomic scale, PDF analysis of X-ray total scattering data is employed. The experimental *in situ* PDFs for the 1st discharge, 1st charge, and 2nd discharge are shown in Figure 5.14a, b, and c respectively. The corresponding electrochemistry for the 1st discharge is shown in Figure 5.15. Note that the electrochemistry shows a higher overpotential than that obtained from a regular coin cell or the *in situ* XANES experiment. This is attributed to the higher current rate (C/20) used in the *in situ* PDF measurement, although the different cell design may also result in the increased overpotential.

The data at the beginning of the discharge, Li = 0, is dominated by the PDF of the CuF<sub>2</sub> phase (Figure 5.14a). The two peaks at 1.9 Å and 2.3 Å, which correspond to the four
equatorial and two elongated axial Cu-F bonds, respectively, reflect the JT distortion for Cu<sup>2+</sup>  $(3d^9)$ . The broad features around 3.6 Å correspond to the distances between the Cu<sup>2+</sup> and the Cu<sup>2+</sup> and F<sup>-</sup> ions in the neighbouring octahedra. Analysis of the *in situ* data indicates a particle size of about 7.0 nm for pristine CCN-CuF<sub>2</sub>, whereas the structural refinement against *ex situ* PDF for pristine CCN-CuF<sub>2</sub> indicates a size of 8.3 nm, both of which are quite consistent with the value obtained in the Scherrer analysis.



Figure 5.15 The phase mole fractions from the final structure refinement against the PDFs on the 1st discharge shown in Figure 5.14a. The white potential profile illustrates the corresponding potential curve for the *in situ* battery.

The PDF for the end of the discharge, Li = 2.0, has peaks at 2.6, 3.6 and 4.4 Å which match the Cu-Cu distances in the 1st, 2nd and 3rd coordination shell for the face-centered cubic (fcc) Cu phase, indicating the formation of Cu metal. No additional atom pairs from other phases were observed. The phase transformation from CuF<sub>2</sub> to Cu is evident in the reduction of the peak intensity for the CuF<sub>2</sub> phase and the growth in intensity for Cu metal.

The phase mole fractions and the evolution of the particle sizes upon discharge were evaluated from the refinement of structural models against the corresponding PDFs, where a bimodal distribution of "small" and "large" Cu particles was employed as the simplest model to describe a non-uniform particle size for the Cu phase.<sup>135</sup> Initial refinements varied particle size to establish an appropriate constraint for particle size and more reliable phase fractions in the final structure refinement. The result of this refinement (Figure 5.16) shows that the small Cu particles increase in size from 0.7 to 2 nm and then stop growing after a capacity of Li = 1.0 is reached. In contrast, the size for large Cu particles is greater than 10 nm, and their size

is larger than can be reliably determined from the X-ray PDF data. The CuF<sub>2</sub> particle size remains essentially unchanged.



Figure 5.16 The evolution of the particle sizes from the initial structure refinement (no particle size constraints applied) against the PDFs on the 1st discharge shown in Figure 5.14a.



Figure 5.17 Pink crosses denote the discharged states where the samples were collected for *ex situ* experiments. The CuF<sub>2</sub> mole fractions are extracted from the LCA of the *ex situ* XANES (red triangles) data and the structural refinements using the *ex situ* PDFs (blue squares). The LiF mole fractions (relative to the amount of LiF at the end of discharge) are evaluated from the integration of normalized <sup>7</sup>Li (green circles) and <sup>19</sup>F (orange inverted triangles) NMR spectra shown in Figure 5.25 (the <sup>19</sup>F data is scaled by a factor of 0.67 in order to draw a direct comparison between the LiF mole fractions obtained from the <sup>7</sup>Li and <sup>19</sup>F NMR).

The final structure refinement was then performed with the size of the CuF<sub>2</sub> and small Cu particles being constrained to 7 and 2 nm, respectively, while the size of large Cu particles was not refined. The final CuF<sub>2</sub> phase fractions of CuF<sub>2</sub> (Figure 5.15) show a trend that is consistent with in situ XANES LCA results: upon discharge, the CuF<sub>2</sub> reacts forming mostly small Cu particles. The conversion of CuF<sub>2</sub> starts to slow down around Li = 1.0. About 12% of the CuF<sub>2</sub> is left when the theoretical capacity is reached. To examine the reaction at even lower potentials, *ex situ* PDF was performed on samples with capacities beyond those expected based on the CuF<sub>2</sub> conversion reaction, *i.e.*, Li = 3.0 and Li = 4.9 which correspond to discharge voltages at 0.75 V and 0 V respectively. The CuF<sub>2</sub> mole fraction from the structure refinement against the corresponding PDFs is shown in Figure 5.17, which shows that CuF<sub>2</sub> fraction remains essentially constant in this voltage window (*i.e.*, during process E).



Figure 5.18 Phase mole fractions upon (a) 1st charge and (b) 2nd discharge obtained from the structure refinements against the corresponding PDFs (Figure 5.14b and c). The potential profiles are shown in white.

The PDFs for the 1st charge (Figure 5.14a) and 2nd discharge (Figure 5.14b) show only small changes that are dominated by the evolution of the Cu metal phase. Even though no discernible atom pairs from the CuF<sub>2</sub> phase are readily observed, a structure refinement using Cu metal and CuF<sub>2</sub> phases reveals an increase of 12.5% in CuF<sub>2</sub> phase fraction for the 1st charge (Figure 5.18a), and a decrease of 8% for the 2nd discharge (Figure 5.18b). Note that any ionic Cu(I) or Cu(II) species present in the liquid electrolyte will also contribute to the PDF, but will only give rise to peaks from any directly bound Cu-X (X = F, O) species. These correlations are difficult to separate from the 1st Cu-F correlation in the solid CuF<sub>2</sub> phase. Therefore, the structural model used for the PDF refinement includes only solid Cu and CuF<sub>2</sub> phases, even though the XANES analysis suggests that a small amount of Cu(I) is present at intermediate states of charge. To gain a better understanding of the cycling behaviour of the HBM CCN-CuF<sub>2</sub> electrode, a second *in situ* cell was cycled at a C/10 current rate. This experiment allows the structural changes of the HBM CCN-CuF<sub>2</sub> electrode during the first four discharge/charge cycles to be observed under *in operando* conditions (Figure 5.19a). The electrochemistry for this battery shows a very similar potential profile but with a slightly higher overpotential as compared with the cell cycled at a C/20 rate in the previous experiment. The change of current rate alters the kinetics of the reaction, without appearing to change the reaction pathway significantly.



Figure 5.19 (a) Selective *in situ* PDFs for CCN-CuF<sub>2</sub> measured for 4 cycles. Only the PDFs for the beginning and the end state of each cycling steps are shown. (b), (c) Differential PDFs on each discharge (b) and charge (c) step, obtained by subtracting the PDF of the end state from the PDF of the beginning state of each cycling step. Black and red arrows indicate the atom pairs corresponding to the Cu and CuF<sub>2</sub> phases, respectively.

The Cu phase is the major contribution to all the patterns obtained at the end of discharge and charge. The intensities of the Cu-Cu correlations (at 2.5 and 4.3 Å) increase in the PDF patterns at the end of discharge as a function of cycle number, decreasing slightly on charge. A small broad feature at around 2 Å for the end of 1st charge is observable, suggestive of an oxidized copper phase. Very small positive shifts (varying between ~ 0.02 and 0.05 Å) in the peak positions of the PDFs due to Cu are observed between the end of charge and those

at the end of discharge, which may be related to differences in the size of the Cu particles. These shifts are not caused by the growth of a Cu phase on the anode. If this phase were present, it would be located at a different (larger) sample-to-detector distance due to the geometry of the *in situ* experiment and AMPIX cell. This would result in small negative shifts of the Cu-Cu correlations as compared to those observed for Cu formed on the positive electrode.

The phase evolution can be seen more clearly by following the differential PDFs, obtained by subtracting the beginning from the end of each discharge or charge, where positive peaks indicate that phase(s) are being formed while the negative peaks represent the phase(s) that are reacting in each discharge (Figure 5.19b) and charge (Figure 5.19c) processes. In Figure 5.19b, the three positive peaks corresponding to Cu-Cu correlations in the 1st, 2nd and 3rd coordination shell of an fcc-Cu phase show the formation of Cu metal upon each discharge step. However the magnitude of the peaks is drastically reduced in the subsequent discharge steps, indicating that less Cu forms in the corresponding process. This is consistent with the decrease in specific capacity of the corresponding discharge steps in the electrochemistry. The negative peak at 1.9 Å, from the equatorial Cu-F bond length in the distorted  $CuF_6$  octahedron, reflects the reduction of the  $CuF_2$  phase. This peak is evident in the 1st discharge, less pronounced in the 2nd discharge, and absent in the 3rd and 4th discharge steps, suggesting a negligible  $CuF_2$  conversion in the subsequent discharge cycles. For the charge steps shown in Figure 5.19c, a similar phenomenon is seen where  $CuF_2$  is only involved in the reaction for the first two charge steps, while Cu oxidation without forming CuF<sub>2</sub> dominates the subsequent charge processes. Comparing the magnitude of the differential PDFs within each cycle, more Cu formation during discharge is observed than Cu oxidation upon charge.

#### 5.3.5 NMR

The composition of HBM CCN-CuF<sub>2</sub> was studied by <sup>19</sup>F MAS NMR and <sup>19</sup>F  $\rightarrow$  <sup>13</sup>C CP-MAS NMR spectroscopy. Figure 5.20 shows the normalized <sup>19</sup>F MAS NMR spectrum of commercial CuF<sub>2</sub> and the CCN-CuF<sub>2</sub> nanocomposite. The <sup>19</sup>F signal of CuF<sub>2</sub> is not detectable because F is directly bound to the paramagnetic Cu<sup>2+</sup> ion.<sup>133</sup> The spectrum of commercial CuF<sub>2</sub> shows only one isotropic resonance at -190 ppm, which is also present in the spectrum of the HBM nanocomposite sample. This signal was ascribed to HF adsorbed on the surface in a previous <sup>19</sup>F NMR study.<sup>163</sup> Three new isotropic resonances at 33, -106, and -147 ppm



Figure 5.20 Normalized <sup>19</sup>F MAS NMR spectra of the commercial  $CuF_2$  (red) and HBM CCN-CuF<sub>2</sub> (blue). Signals marked with asterisks are spinning side bands. No <sup>19</sup>F signal background from the rotor is observed.

are present in the HBM sample, which are most likely related to the additional phases formed during the ball-milling procedure. For the preparation of the CCN-CuF<sub>2</sub> sample, commercial CuF<sub>2</sub> was mixed with carbon black and then ball-milled in a zirconia jar with zirconia beads. The collision between the milling beads and the milling jar is very likely to introduce a zirconium-containing component into the nanocomposite. Therefore, the resonance at 33 ppm in the HBM sample is tentatively assigned to  $\beta$ -ZrF<sub>4</sub><sup>164</sup> or a zirconium oxyfluoride<sup>165</sup>, as a result of the reaction with CuF<sub>2</sub>. A Cu(I) species was observed in the XANES spectra (Figure 5.8), providing evidence for Cu(II) reduction during the ball-milling process. Such reduction reaction can occur in the presence of the reducing agent carbon under elevated temperatures induced by the ball-milling: CuF<sub>2</sub> + C  $\rightarrow$  CuF<sub>2-x</sub> + CF<sub>x</sub>. The resonances at -106 and -147 ppm in the HBM sample are thus assigned to  $-CF_2$  and -CF fluorinated  $sp^2 C$  sites respectively, on the basis of prior <sup>19</sup>F MAS NMR studies of fluorinated carbon.<sup>166,167,168</sup> The assignment is further confirmed by <sup>19</sup>F  $\rightarrow$  <sup>13</sup>C CP-MAS NMR experiments (Figure 5.21) where a broad <sup>13</sup>C signal between 50 to 100 ppm is evident, similar to the <sup>13</sup>C chemical shift of graphite fluorides,<sup>168</sup> demonstrating that at least some of the fluorine species are in close spatial proximity to the carbon.



Figure 5.21 <sup>19</sup>F  $\rightarrow$  <sup>13</sup>C CP-MAS NMR spectrum of HBM CCN-CuF<sub>2</sub>. No signal was present in the spectrum when the <sup>19</sup>F CP pulses were removed.

A series of cycled samples were investigated by <sup>7</sup>Li and <sup>19</sup>F MAS NMR, to investigate the evolution of LiF phase, as well as to shed light on the formation of SEI products. The normalized <sup>7</sup>Li and <sup>19</sup>F NMR spectra are shown in Figure 5.22a and b, respectively. (The <sup>19</sup>F NMR for Li = 0.04 is enlarged in Figure 5.23.) Only one resonance is observed in the <sup>7</sup>Li MAS NMR spectra, while more than one resonance is present in the <sup>19</sup>F MAS NMR spectra. For <sup>7</sup>Li MAS NMR, a small resonance is observed at -0.7 ppm even on the pre-plateau before the Cu/LiF nucleation potential dip<sup>169</sup> (region A of the voltage curve (Figure 5.3)) (Li = 0.04). The peak shifts to -2.2 ppm at Li = 0.5, and then shifts back to -1.7 ppm between Li = 0.5 and 2.0. On charge, the resonance keeps shifting towards higher ppm, reducing in intensity until the potential of the corresponding sample reaches about 3.92 V. This is followed by an increase in intensity until the end of charge. There are few Li species that give rise to negative chemical shifts other than LiF at -1.0 ppm.<sup>170</sup> A resonance at -2.2 ppm was similarly reported in our earlier study of CuF<sub>2</sub>, for Li = 0.5 on discharge. The resonance was assigned to LiF, the lower frequency shift being attributed to the formation of either nano-sized or a thin film of LiF in close proximity to either Cu metal or CuF<sub>2</sub>.<sup>133</sup>



Figure 5.22 Normalized (a) <sup>7</sup>Li and (b) <sup>19</sup>F MAS NMR spectra of cycled CCN-CuF<sub>2</sub>. Signals marked with asterisks are spinning side bands. The inserts show the overlay plots of the isotropic resonances of the corresponding spectra. Numbers in the inserts are the values of the chemical shifts. ("Li x.x" represents the specific capacity on discharge; "x.x V" refers to the potential on charge where the batteries were stopped for measurement.)

As the reaction proceeds, the LiF particle size becomes larger and the LiF shift is less affected by the Cu metal/CuF<sub>2</sub> (*i.e.*, a larger portion of the LiF phase is not in close proximity to Cu/CuF<sub>2</sub>), accounting for this shift to more positive frequencies as lithiation proceeds. The increase in Li intensity at the late state of discharge is ascribed to the formation of products from LiPF<sub>6</sub> hydrolysis or electrolyte decomposition such as Li<sub>2</sub>CO<sub>3</sub> and Li<sub>2</sub>PO<sub>x</sub>F<sub>y</sub>, as suggested by our CV study, these species giving rise to more positive <sup>7</sup>Li chemical shifts,<sup>170-</sup><sup>171</sup> leading to a shift towards higher frequencies at the top of charge.



Figure 5.23 <sup>19</sup>F MAS NMR for discharged CCN-CuF<sub>2</sub> sample at Li = 0.04, a magnification of the spectrum of the same sample shown in Figure 5.22b. Signals marked with asterisks are spinning side bands.

A similar intensity evolution is observed in the <sup>19</sup>F NMR spectra but now the spectra are not complicated by the potential overlap between LiF and any other electrolyte decomposition products. For the discharged sample Li = 0.04, three resonances are present (Figure 5.23) which are assigned to LiPF<sub>6</sub> (-80 ppm), CF<sub>x</sub> (-147 ppm) and LiF (-204 ppm). The LiF resonance at -204 ppm dominates the spectra and the evolution of its chemical shift and intensity follow the same trend as the <sup>7</sup>Li NMR resonance, confirming that the <sup>7</sup>Li signal can be largely ascribed to LiF. The resonance for CF<sub>x</sub> at -147 ppm becomes poorly resolved on cycling, while a new resonance at -78 ppm starts to evolve at higher potential than 3.92 V upon further charge, which is assigned to Li<sub>2</sub>PO<sub>3</sub>F according to an NMR study on the hydrolysis of LiPF<sub>6</sub>.<sup>171</sup>

Interestingly, the LiF phase formed at the early state of discharge Li = 0.04 before the Cu nucleation step is probably not associated with the formation of the metallic Cu phase but is rather associated with a reaction with the fluorinated carbon components. The Li uptake mechanism for carbon fluorides  $CF_x$  depends on the nature of the C-F bond.<sup>172</sup> Our <sup>19</sup>F NMR for the pristine CCN-CuF<sub>2</sub> reveals an  $sp^2$  character for the carbon in the CF<sub>x</sub> phase, the carbon incorporating Li at a higher potential (~ 3.2 V) via the reaction:  $CF_x + nLi \rightarrow (1-n) CF_x + nC + nLiF$ , in comparison to the CF<sub>x</sub> with a  $sp^3$  carbon (~ 2 V).<sup>37</sup> The lithiation potential of the

ionic CF<sub>x</sub> is consistent with the potential of the pre-plateau feature A in the electrochemistry curve (Figure 5.3).<sup>172</sup> Such fluorinated carbon phase should also be in very close proximity to carbon matrix since it is derived directly from the carbon. This means that the CF<sub>x</sub> should be more effectively electrically wired than CuF<sub>2</sub>. Note that the LiF formed in the reaction with CF<sub>x</sub> is surrounded by carbon, which results in a <sup>7</sup>Li chemical shift (-0.7 ppm for sample Li = 0.04) that is closer to LiF's reported value (-1.0 ppm<sup>170</sup>).



Figure 5.24 <sup>7</sup>Li (red) and <sup>19</sup>F (blue)  $T_1$  measurements for the samples shown in Figure 5.22. The electrochemical potential profile is shown for comparison.

<sup>7</sup>Li and <sup>19</sup>F  $T_1$  measurements were performed on the same series of samples in order to shed light on the particle size evolution of the LiF phase (Figure 5.24) and the trends observed for both nuclei are in agreement with each other. A significant increase in  $T_1$  upon discharge coincides with the sudden drop of potential in the electrochemistry profile, the change being more noticeable between Li = 1.7 to 2.0. A significant reduction of  $T_1$  occurs at the beginning of charge and continues until approximately 3.92 V. These suggest that the LiF particle size increases significantly from Li = 1.0 till the end of discharge; this is followed by a drastic reduction on charging until the potential reaches around 3.8 V.



Figure 5.25 Normalized (a) <sup>7</sup>Li and (b) <sup>19</sup>F MAS NMR spectra of discharged CCN-CuF<sub>2</sub>. Signals marked with asterisks are spinning side bands. <sup>19</sup>F signals at -76 ppm, -124, and -205 ppm are ascribed to  $Li_2PO_3F^{171}$ , rotor background, and LiF respectively.

A more careful quantitative analysis of the <sup>7</sup>Li (Figure 5.25a) and <sup>19</sup>F (Figure 5.25b) MAS NMR spectra on the 1st discharge was performed to separate the contribution from the SEI components and the LiF. To compare the Li and F contents, we first analyse a sample in the region before the onset of any significant side reactions (the Li = 1.0 sample on discharge) and assume that the <sup>7</sup>Li spectrum is dominated by LiF. The relative intensities of the resonances observed in the spectra from the other samples can then be scaled appropriately to extract the (diamagnetic) Li and F mole fractions. The results from this analysis are compared with phase fractions obtained from ex situ XANES and PDF measurements in Figure 5.17. The CuF<sub>2</sub> phase fractions obtained from the LCA analysis of the *ex situ* XANES and the structure refinement of the ex situ PDFs are in excellent agreement, and the trend of LiF phase evolution evaluated from the <sup>19</sup>F NMR mirrors the negative trend observed in the XANES and PDF data. This good match suggests that the formation of LiF is mainly the result of the CuF<sub>2</sub> conversion. The nominal LiF content obtained by <sup>7</sup>Li NMR is very different and tracks the overall Li content determined electrochemically. This observation confirms that electrolyte decomposition dominates at low potentials producing SEI components (other than LiF) that also contribute to the <sup>7</sup>Li signal. A <sup>31</sup>P MAS NMR spectrum of a sample extracted from a fully discharged battery at around 1 V (Figure 5.26) shows two resonances at 1 and -150 ppm, which can be assigned to  $Li_3PO_4$  and  $LiPF_6$ , respectively.<sup>171</sup> The presence of  $PF_6^-$  is also observed in the early state of discharge Li = 0.04 (Figure 5.23), and is mostly due to  $LiPF_6$ residue from the electrolyte. The observation of  $PO_4^{3-}$  demonstrates that Li<sub>3</sub>PO<sub>4</sub> is the main phosphate-containing product of electrolyte salt hydrolysis/degradation.



Figure 5.26 <sup>31</sup>P MAS NMR spectrum of fully discharged CCN-CuF<sub>2</sub> (Li = 2.0).

#### 5.4 Reaction Mechanisms

#### 5.4.1 Discharge

We now combine all of the results to discuss the various mechanisms that occur in this system. At the beginning of the discharge, a CF<sub>x</sub> phase (identified by <sup>19</sup>F MAS and <sup>19</sup>F  $\rightarrow$  <sup>13</sup>C CP-MAS NMR spectroscopy) reacts with Li<sup>+</sup> prior to the onset of the CuF<sub>2</sub> conversion, giving rise to the pre-plateau A at around 3.1 V (Figure 5.3). Upon further discharge, both *in situ* XANES and *in situ* PDF demonstrate a straightforward two-phase reaction mechanism for CuF<sub>2</sub> conversion, CuF<sub>2</sub> + Li  $\rightarrow$  Cu + 2LiF. No evidence for a Cu(I) species, possibly formed via Li intercalation, is observed in the early state of discharge in either the 1st derivative of the difference XANES spectra (Figure 5.9c) or the CV study, where only one reduction peak B is present. Furthermore, no resonances corresponding to a Li<sub>x</sub>CuF<sub>2</sub> phase are seen in either the <sup>7</sup>Li or <sup>19</sup>F MAS NMR spectra. Therefore, a stable Li<sub>x</sub>CuF<sub>2</sub> intermediate phase, as proposed in the CuF<sub>2</sub>-thin-film study<sup>173</sup>, is not formed in the CCN-CuF<sub>2</sub> electrode on discharge.

As the CuF<sub>2</sub> conversion proceeds, the operating potential starts to slope down at around Li = 1.0 and small features  $B_H$ , C (Figure 5.3) and D (Figure 5.6) are observed (see the GITT results (Figure 5.4)). According to the Gibbs phase rule, a two-phase reaction under constant temperature and pressure should theoretically exhibit a flat potential plateau.<sup>91</sup> There is no evidence for a change in the mechanism of the conversion reaction (and a change from two-phase to single-phase (solid solution)) at Li = 1. Rather, the conversion reaction is

associated with a larger overpotential at this point. This drop in potential enables additional side reactions ( $B_H$ , C and eventually D) to occur, and since the kinetics of these reactions are faster, they increasingly predominate over the conversion reaction.

	1st D	bischarge	1st Charge					
Α	3.3 V*	CF <sub>x</sub> lithiation	<b>B</b> <sub>1</sub> '	3.58 V*	Cu(0) to Cu(I)			
В	3.25 V <sup>#</sup>	$CuF_2$ one-step lithiation forming Cu + 2LiF			Cu(I) to Cu(II) or			
B <sub>H</sub>	2.5 V <sup>‡</sup>	reaction of the hydrated CuF <sub>2</sub> phase	<b>B</b> <sub>2</sub> '	3.8 V*	Cu(0) to Cu(II) oxidation			
С	1.7 V*	electrolyte (mainly DMC) decomposition on Cu surface	C'	3.2 V*	oxidation of SEI formed in process C			
D	0.65 V*	electrolyte (EC/DMC) decomposition on carbon surface	D,	4.4 V*	oxidation of SEI formed in process D			
E	0.4 - 0 V*	reactions related to carbon	<b>E</b> '	~ 1.0 V*	reaction related to carbon, correlated with process E			

Table 5.2 Assignments of the labels in the electrochemistry plots. The potentials of these processes extracted from the galvanostatic and CV experiments are given. The equilibrium potential from GITT is given for the main conversion reaction.

Feature  $B_H$  in the electrochemistry is always indistinct and sometimes not observed. Furthermore, it is only observed in the first discharge, suggestive of an irreversible process. The potential where this reaction occurs is higher than generally expected for electrolyte decomposition. We therefore ascribe it to the Li reaction with the hydrated CuF<sub>2</sub> phases. As discussed in the CV section, features C and D (Figure 5.5 and Figure 5.6) are attributed to the electrolyte decomposition on copper and carbon surfaces, respectively. The occurrence of electrolyte side reactions below 2 V is further verified by the comparison of total Li mole fraction (LiF and additional lithiated SEI components) obtained from *ex situ* <sup>7</sup>Li and the LiF mole fraction obtained by <sup>19</sup>F NMR (Figure 5.17). Electrolyte decomposition results in Li salts (such as LiF, LiOCO<sub>2</sub>R, Li<sub>2</sub>CO<sub>3</sub>,<sup>147,154</sup> and Li<sub>3</sub>PO<sub>4</sub>) that passivate the electrode surface, the presence of Li<sub>3</sub>PO<sub>4</sub> being confirmed by <sup>31</sup>P NMR. LiOCO<sub>2</sub>R, Li<sub>2</sub>CO<sub>3</sub>,<sup>147,154</sup> and Li<sub>3</sub>PO<sub>4</sub> give rise to <sup>7</sup>Li resonances that are higher in frequency than the shift of LiF (-1 ppm),<sup>170</sup> resulting in an overall shift of the <sup>7</sup>Li resonance to higher frequencies beyond Li = 1. In the subsequent CV sweeps (Figure 5.7b), less Cu is formed on reduction, and so less electrolyte decomposition on the Cu surface is expected. This is reflected by an intensity reduction/absence of peak C in association with the intensity reduction/absence of peak B; additionally, smaller currents are observed for peaks D and D', suggesting that the SEI layer on the carbon surface prevents further electrolyte decomposition.

In addition to the side reactions taking place after the kink in the electrochemical curve (at Li = 1.0), a distinct change in the rate at which the Cu and LiF particles grow in size are indicated by the structure refinements using the PDF data (Figure 5.16a) and NMR  $T_1$  measurements (Figure 5.24). Previous high resolution transmission electron microscopy (HRTEM) studies on the pristine CCN-CuF<sub>2</sub> prepared using the same HBM technique reveal 8 nm CuF<sub>2</sub> nanoparticles present as large agglomerations (50 – 100 nm),<sup>135</sup> consistent with our measurements of an average particle size of 8.3 nm (PDF) and 10 nm (Scherrer analysis, XRD) for our system. The Scherrer equation gives a volume-weighted size, while the PDF measurement is weighted by the mole fraction, accounting for the difference in the two measured values.<sup>174</sup> Upon discharge, no significant change in the CuF<sub>2</sub> crystallite size extracted from the *in situ* PDF is observed. The size of the LiF phase, as reflected by the NMR  $T_1$  measurements, does not change noticeably at the beginning of discharge, while the size of the small Cu nanoparticples, and the concentration of larger (> 10 nm) particles increases according to the structure refinements of the corresponding PDFs.

We also observed a noticeable increase in overpotential at Li = 1.0 in our previous studies of the CuF<sub>2</sub> system, with slightly larger CuF<sub>2</sub> particles (approx. 16 nm).<sup>133</sup> In that study, the rising overpotential was accompanied by a loss in crystallinity of the entire CuF<sub>2</sub> component, which we ascribed to particle cracking, possibly caused by Cu formation within these larger particles. A similar phenomenon is not seen here, possibly because the individual particles are slightly smaller. Furthermore, there is no reduction of CuF<sub>2</sub> particle size as the reaction proceeds, suggesting that particles largely react one by one, so that we do not see any clear evidence for any shrinking in the size of the CuF<sub>2</sub> nanoparticles. This is in agreement with recent *in situ* TEM studies of FeF<sub>2</sub> particles, where the particles were seen to react sequentially from the outside to the inside of both the original FeF<sub>2</sub> particle and the whole FeF<sub>2</sub>-C agglomerate.<sup>137</sup>

As discussed in our prior work<sup>133</sup>, the nucleation and growth of the different phases that form during the conversion reactions, and thus the morphologies and sizes of the particles within the nanocomposites, are governed by a number of factors which include (i) the relative

rates of diffusion of the cations, anions and Cu atoms/ions through the original starting material, (any) intermediate phases, the final salts (LiF and SEI), and in the grain boundaries/interfaces between these phases, and (ii) the electronic conductivities of the different components.<sup>40</sup> Li<sup>+</sup> ion diffusion in both CuF<sub>2</sub> and LiF is expected to be poor, but fluoride diffusion within the  $CuF_2$  phase cannot be ruled out.  $CuF_2$  is a poor electronic conductor, and hence the Cu metal (and carbon) morphologies dictate the electronic wiring of the composite. No intermediate phases are present in this system, although the CuF<sub>2</sub>/Cu/LiF triple phase boundary, where Cu reduction occurs, will consist of poorly crystalline phases with poorly defined stoichiometries. The first CuF<sub>2</sub> particles to be reduced are those in direct or close contact to the carbon particles, due to the poor electronic conductivity of  $CuF_2$ . Copper is extruded from the particles and nanoparticles of LiF are formed. The LiF phase is in close contact to the Cu and CuF2 surfaces, as suggested by <sup>7</sup>Li and <sup>19</sup>F MAS NMR where a more negative chemical shift for the LiF signal is observed in the early state of discharge. Some fluoride ion migration may also occur through  $CuF_2$  (as suggested previously) resulting in LiF coating of the entire reacting CuF<sub>2</sub> nanoparticle.<sup>133</sup> The formation of LiF should intrinsically lead to a higher overpotential due to its poor electronic conductivity. However, the formation of more Cu yields a larger interfacial area for the conversion reaction to take place. The reaction continues, consuming particles buried more deeply in the agglomerate, promoted by the Cu wiring.

As the reaction approaches the kink position (Li = 1.0), LiF increasingly covers the  $CuF_2$  and Cu nanoparticles leading to a larger overpotential due to LiF's poor electronic conductivity and low Li<sup>+</sup> diffusivity. Furthermore, the reaction front has moved deeper into the composite, increasing the electronic and ionic resistance associated with (i) the electronic wiring that connects the carbon (the source of electrons) and the reduction front, and (ii) the ionic transport of the Li<sup>+</sup> ions from the electrolyte to the  $CuF_2$  reaction front. The relative position of the kink (increasing overpotential) is probably related to the size of the  $CuF_2$  agglomerate, the  $CuF_2$  particle sizes, and the nature of the carbon-Cu wiring. Some sintering must occur as Cu particles larger than the size of the original  $CuF_2$  particles are observed in the *in situ* PDF measurements. These are a minority component, particularly during the early stages of the conversion reaction, suggesting that the observation of large particles in prior *ex situ* XRD studies<sup>133</sup> may in part be a consequence of particle aging. However, the sintering increases as the reaction proceeds, which may lead to disconnected Cu particles (*i.e.*, particles not wired to the carbon matrix), as also observed in the previous TEM study of fully

discharged  $CuF_2$ .<sup>135</sup> The presence of disconnected Cu particles may also increase the overpotential since the  $CuF_2$  particles in the core of the agglomerate are no longer wired to the carbon.

When the operating potential decreases till below 2.0 V and 1.0 V, the electrolyte starts to decompose on the Cu and carbon surface successively, with each forming a passivating layer leading to an even larger polarisation. This results in an even more difficult electronic and ionic transport, and consequently a continuous increase in the overpotential. Furthermore, the conversion reaction results in a volume change of about 29% based on the crystalline densities, which will result in an expansion of the agglomerate. This expansion may result in cracks, exposing fresh surfaces for electrolyte decomposition and breaking Cu-Cu contacts, both increasing the overpotential. Eventually, when the electron transport pathways are all terminated by LiF and SEI products, the electrons and Li<sup>+</sup> ions can no longer reach the core of the initial CuF<sub>2</sub> agglomerate, leaving behind a small amount of unreacted CuF<sub>2</sub> in the center of the agglomerate. Further discharging to 0 V only induces more electrolyte reactions associated with carbon, but does not reduce the amount of unreacted CuF<sub>2</sub>.

#### 5.4.2 Charge



Figure 5.27 Potential profile obtained on charging a cell using Cu foil as the cathode. The process taking place at the 3.5 V plateau is attributed to the Cu dissolution.

Upon charge, four different processes can be distinguished in the potential curve and CV (Figure 5.3 and Figure 5.5), labelled as C', B<sub>1</sub>', B<sub>2</sub>', and D'. It has been reported that Cu metal dissolves in a wide range of organic solvents without passivation, mainly as  $\text{Cu}^+$ .<sup>175,176</sup> Depending on the electrolyte, the dissolution voltage varies between 3.5 V - 3.7 V vs. Li/Li<sup>+, 177</sup> For example, the thermodynamic equilibrium potential for the reaction: Cu  $\rightarrow$  Cu<sup>+</sup> + e<sup>-</sup> in an aqueous solution under standard conditions is 3.566 vs. Li/Li<sup>+147</sup> and a corrosion potential of 3.6 V was observed in a 1 M LiPF<sub>6</sub>/EC-DEC electrolyte.<sup>178</sup> Our battery, using Cu foil as cathode, shows a dissolution plateau at a similar voltage (3.5 V) (Figure 5.27). Thus, we ascribe peak B<sub>1</sub>' at 3.58 V to Cu(0) to Cu(I) oxidation and B<sub>2</sub>' to the Cu(I) to Cu(II) or simultaneous Cu(0) to Cu(II) oxidation, in agreement with our in situ XANES analysis. Regarding the form of the dissolution products, a prior study revealed that the dissolution of Cu is not associated with any solid deposition formation.<sup>177</sup> This is consistent with our PDF results, where no clear evidence for the presence of a third phase other than Cu and CuF<sub>2</sub> is observed either in situ or ex situ. The phase evolution from the PDF structure refinements and differential PDFs demonstrates only a small growth of the CuF<sub>2</sub> phase in the first two charge steps. The <sup>7</sup>Li and <sup>19</sup>F NMR and the  $T_1$  result indicate a significant reduction in both quantity and the grain size of LiF upon charge before the rising-voltage region D' is reached. This suggests that a reaction consuming a large amount of LiF is taking place at B<sub>1</sub>' and B<sub>2</sub>'. Studies on copper dissolution have revealed that the presence of impurities such as H<sub>2</sub>O and HF, which facilitate the hydrolysis of LiPF<sub>6</sub> forming LiF, may considerably enhance the dissolution of Cu.<sup>147, 179</sup> These prior studies correlate the reduction of LiF phase fraction with Cu dissolution, suggesting the dissolution is associated with F<sup>-</sup> anions. As shown in the PCA analysis of the XANES spectra, upon oxidation of Cu to Cu<sup>+</sup>, a tetrahedrally-coordinated Cu(I) complex ion such as  $[Cu(I)F_4]^{3-}$  (with Cu environment similar to that found in CuCl) appears to be present. On further oxidation to  $Cu^{2+}$ , a Cu(II) species, the majority of which has a Cu local environment similar to that found in  $CuF_2$  is formed, possibly  $[Cu(II)F_6]^{4-}$ . On the basis of the combined capacity of regions B<sub>1</sub>' and B<sub>2</sub>', dissolution of approximately 30% of the Cu is expected, assuming that no other reactions occur at this voltage. If we then assume that the final dissolution product is  $[Cu(II)F_6]^{4-}$ , this copper dissolution consumes about 90% of the total amount of LiF, in order to form the complex ion  $[Cu(II)F_6]^{4-}$ . This rough calculation, however, is consistent with the almost complete loss of the LiF phase observed in the aforementioned <sup>7</sup>Li and <sup>19</sup>F MAS NMR, confirming that the Cu dissolution process consumes LiF. This therefore prevents CuF<sub>2</sub> reconversion from taking place even at a potential as high as 4.5 V. It is worth noting that when the batteries were disassembled for ex situ experiments,

a Cu<sup>2+</sup>-type greenish blue and/or a lustreless brown was sometimes noticed on the lithium metal, suggestive of the Cu<sup>2+</sup> ion migration, and/or possibly Cu re-deposition.<sup>147</sup> However, the formation of negatively charged copper (I) and (II) ions most likely helps to reduce the extent of the redox shuttle mechanism involving Cu deposition.<sup>147</sup>

Interestingly, a decrease in the current associated with feature B<sub>1</sub>' in the CV plot (Figure 5.5) is associated with an increase in the current associated with feature C', C' being correlated with the reduction peak C in the anodic sweep. However, the current magnitude for feature B<sub>2</sub>' does not change significantly. Feature C has been attributed to the electrolyte decomposition and formation of a passivating SEI layer on the Cu surface. The presence of such a passivating layer impedes the oxidation process  $B_1$ ', suggesting that the corresponding reaction from Cu(0) to Cu(I) is probably a kinetically controlled process. However, the formation of Cu(II) species is less affected. The assignment of reaction C' to the decomposition of the SEI formed during process C, is further supported by NMR results. The <sup>19</sup>F NMR on the sample collected at the charge state of 3.22 V (Figure 5.22b), which is just after the feature C' in the potential curve, shows about the same intensity as the one for the end of discharge Li = 2.0, suggesting the majority of LiF does not participate in process C'. By contrast, the <sup>7</sup>Li NMR data for the same sample reveals a noticeable intensity reduction as compared to the end of discharge, indicating a decrease in the Li containing components. These observations reflect a reduction in the amount of non-LiF components being associated with the degradation of the SEI formed on Cu surface. <sup>7</sup>Li and <sup>19</sup>F NMR confirm that LiF and Li<sub>2</sub>PO<sub>3</sub>F are formed during process D' due to electrolyte decomposition. The correlation between processes D' and D (SEI formation on carbon surface), suggests that the newly formed LiF is in close contact with carbon, rather than Cu metal. Therefore very little amount of this LiF phase will participate in the Cu dissolution or the Cu oxidation to form CuF<sub>2</sub>. The unreacted CuF<sub>2</sub> left after the 1st discharge can presumably react in the second cycle in part because the Cu and LiF dissolution removes some of the passivating LiF coating.

Many factors, such as ionic diffusion, electron transport, volume expansion, and SEI formation, are known to have a great impact on the reversibility of conversion reactions. In this specific case, however, the main reason for the poor reversibility is shown to be Cu dissolution and simultaneous LiF consumption. This should be contrasted with the highly reversible fluoride system FeF<sub>2</sub>. The potential for FeF<sub>2</sub> reconversion upon charge (~ 3.0 V) is far outside of the dissolution potential range (~ 4.0 - 4.6 V depending on the electrolyte composition and the type of salt) for Fe metal.<sup>37,135,177</sup> In contrast to Fe, the dissolution

potential for Cu metal (~ 3.5 - 3.7 V) in an electrolyte composed of organic carbonates is about the same value as the theoretical potential for CuF<sub>2</sub> (3.55 V). Consequently, in the presence of the overpotentials that are typical for conversion reactions, Cu dissolution will take place and compete with the reconversion reaction: Cu +  $2\text{LiF} \rightarrow \text{CuF}_2$ , consuming the majority of the LiF phase formed upon discharge. Approaches should, therefore, be taken to prevent the dissolution from taking place, by for example (i) using appropriate surfacecoatings and/or additives to the electrolyte to enhance the stability of Cu metal at high potentials, and (ii) replacing the organic solvent and salt with an electrolyte system that will not facilitate the Cu dissolution. The latter is challenging due to the often very similar solubilities of Li<sup>+</sup> and Cu<sup>+</sup>.

#### 5.5 Conclusions

An investigation of the conversion reaction mechanism for carbon-coated CuF<sub>2</sub> has been performed with an array of characterization tools providing a comprehensive understanding of the reaction for multiple discharge/charge cycles. CV experiments and *in situ* XANES reveal multiple redox pairs including a one-step lithiation step on discharge to form Cu directly and a two-step Cu oxidation on charge involving formation of an intermediate Cu(I) species most likely with a tetrahedral coordination. A correlation between SEI formation/decomposition and the Cu/carbon surface is demonstrated. The Cu(I) species is eventually oxidized to an octahedrally coordinated Cu(II) complex anion. *In situ* PDF sheds light on the phase transformations and reveals that the majority of CuF<sub>2</sub> only participates in the 1st discharge and very little or no CuF<sub>2</sub> formation takes place upon charge. NMR provides insight into the LiF phase, the SEI components and also the impurity phases, *i.e.* CF<sub>x</sub>, which are all challenging to probe by aforementioned techniques. The size evolution of the LiF phase reflected by <sup>7</sup>Li and <sup>19</sup>F NMR *T*<sub>1</sub> measurements provides a link between the growth of LiF particles and the increase in overpotential.

The PDF measurements show that the amount of the small Cu nanoparticles grow at the beginning of the  $CuF_2$  conversion, which enhances the electronic conductivity and helps compensate for the insulating effect from the LiF phase. Since the size of the LiF phase is much bigger than that of Cu metal, the formed Cu is largely covered by an insulating LiF layer, helping to prevent sintering. Eventually this LiF coating serves to reduce Cu-Cu wiring leading to a larger overpotential. In addition, SEI formation on the Cu surface enlarges the overpotential even more and, consequently, a continuous potential reduction is observed on discharge after about 1Li has been inserted per  $CuF_2$  formula unit, even for our best performing electrodes.

The charging mechanism for  $CuF_2$  is fundamentally different from most other conversion materials, because the potential for Cu metal dissolution in an organic electrolyte is close to that of the reconversion reaction. Cu, therefore, dissolves in the electrolyte and consumes the LiF thereby hindering the Cu to  $CuF_2$  transformation. In order to prevent the dissolution from taking place and to transform this material into a practical rechargeable battery system, approaches such as surface coating and/or electrolyte substitution are required to stabilize the Cu metal at high potentials.

### Conclusions

To develop novel materials, three strategies are proposed in this thesis, and each is represented by a case study: i) changing the composition of the materials that are structurally analogous to  $LiCoO_2$ ,  $LiMn_2O_4$  and  $LiFePO_4$  to obtain better capacities (layered  $Li_{1+x}V_{1-x}O_2$ ); ii) nanostructuring conventional materials with new morphologies to improve the capacity and cycling rate (TiO<sub>2</sub>-B nanoparticles); iii) searching for materials that operate via new routes other than insertion mechanism, for a higher energy density (CuF<sub>2</sub> conversion material).

In the studies of those relevant materials, the knowledge of their structures in both short and long ranges is crucial to achieve a fundamental understanding of their reaction mechanisms. The traditional crystallographic method via Bragg diffraction is incapable of delivering local structural information, thereby motivating us to seek alternative methods. To this end, we employed pair distribution function (PDF) via the X-ray total scattering data throughout the studies, incorporated with structure refinement and advanced modelling. Combining the PDF analyses with other structural characterization techniques, *i.e.*, smallangle X-ray scattering (SAXS), X-ray absorption spectroscopy (XAS), and solid state nuclear magnetic resonance (NMR) spectroscopy, enables us to present accurate descriptions of:

i) the structure with local distortions in  $Li_{1+x}V_{1-x}O_2$ :

In the stoichiometric LiVO<sub>2</sub> (x = 0), V atoms displace by 0.17(2) Å from the normal sites of the undistorted  $\alpha$ -NaFeO<sub>2</sub> lattice forming V<sup>3+</sup>–V<sup>3+</sup>–V<sup>3+</sup> trimers, with V-V correlations at 2.54(2) and 3.00(2) Å within and between the trimers, respectively. The distribution of the trimers gives rise to 3 distinct Li environments due to the stacking sequence of V-layers, instead of 2 Li sites as reported previously. As the amount of excess Li increases (x > 0), a higher degree of disorder was suggested by the NMR data, which possibly leads to a better electrochemical performance.

#### ii) the morphology of TiO<sub>2</sub>-B nanoparticles:

The nanoparticles adopt an oblate shape that is contracted along b-axis, with an aspect ratio of 0.68, a major radius of 1.9 nm and a minor radius of 1.3 nm; rather than a previously reported structure which is a prolate spheroid elongated along c-axis. Among various morphologies that had been investigated, such an oblate model facilitates the Li diffusion by offering a

maximum number of diffusion channels per unit volume with a short transport length, thereby significantly enhancing the rate performance.

iii) the reaction mechanism of  $CuF_2$ :

The discharge reaction involves a one-step lithiation of  $CuF_2$  directly forming Cu and LiF. The growth of LiF associated with SEI formation eventually leads to an increasing overpotential. The charging mechanism is associated with Cu metal dissolution, which is fundamentally different from other conversion fluorides. The dissolution takes place via a two-step Cu oxidation involving formation of an intermediate Cu(I) species most likely with a tetrahedral coordination, which further oxidized to an octahedrally coordinated Cu(II) species. Such an oxidation process consumes the majority of LiF, thereby hindering the Cu to CuF<sub>2</sub> transformation. Approaches such as surface coating and/or electrolyte substitution need to be applied to prevent the dissolution from taking place and to transform this material into a practical rechargeable battery system.

# Appendix

### 1. Relationships between the original $\alpha$ -NaFeO<sub>2</sub> and the supercell:



Figure A.1 The relationship between the original and supercell of  $LiVO_2$ . The blue dashed lines show the unit cell of the undistorted structure on *ab*-plane, whereas the green dashed line correspond to the lattice of the distorted (superstructure) model. Red arrow represents the [110] vector in the undistorted lattice. Black dashed lines represent a set of planes in this 2 dimensional representation. These planes are labeled with the Miller indices of the corresponding lattices (again blue = original cell; green = supercell).



Figure A.2 Simulated electron diffraction pattern of the (a) undistorted structure<sup>111</sup> and (b) proposed distorted structure along the [110] zone axis.

The original  $\alpha$ -NaFeO<sub>2</sub> (undistorted) structure (in blue) and superstructure (green) are shown in Figure A.1. Marked on this figure are the (110) planes of the  $\alpha$ -NaFeO<sub>2</sub> structure (in blue) and the (030) planes of the new lattice (in green), which are clearly equivalent. (Note that these planes are lines in the 2D representation.) The equivalency of these planes is confirmed by the simulated electron diffraction pattern in Figure A.2a and b, where the (110) plane in the original lattice shares the same d-spacing with the (030) plane in the new lattice. Similarly, the (1/3 1/3 0) plane in the lattice of the undistorted structure is equivalent to plane (010) in the new lattice (Figure A.1). Due to the reduction of symmetry caused by the V displacements, additional reflections should become observable as shown in Figure A.2b. This is consistent to the electron diffraction pattern published by Tian *et al.*<sup>110</sup>, which clearly shows the {1/3 1/3 0}-type superlattice reflection.

### 2. Refined structure of LiVO<sub>2</sub> with local distortion:

Table A.1 Atomic positions of the 3-layer model supercell obtained with: (a) fixed Li and O positions, but by varying the V positions and unit cell parameters; (b)fixed Li positions, but unconstrained O and V positions and unit cell parameters. The refinements were both performed in the range from  $1.6 \sim 16$  Å to explore short-range structure.

Structure M	l (a)	Space (	Grou	ıp : <i>P</i> 1	Structure Model (b)			Space Group : P1				
a / Å		b /	/ Å		c / Å	a / Å		b /	b / Å		c / Å	
4.9093		4.9093		14.8142		4.90871		4.90871		14.8121		
α/°		<b>β</b> / °			γ/°	α/°		β / °		γ/°		
90		90			120	90		90		120		
Atom	x		у		z	Atom		x	у		z	
Li1	0.00000		0.00000		0.50000	Li1	0.	00000	0.00000		0.50000	
Li2	0.66670		0.33330		0.50000	Li2	0.	66670	0.33330		0.50000	
Li3	0.33330		0.66670		0.50000	Li3	0.	.33330	0.66670		0.50000	
Li4	0.33330		0.00000		0.16670	Li4	0.	.33330	0.00000		0.16670	
Li5	0.00000		0.33330		0.16670	Li5	0.	00000	0.33330		0.16670	
Li6	0.66670		0.66670		0.16670	Li6	0.	.66670	0.66670		0.16670	
Li7	0.66670		0.00000		0.83330	Li7	0.	.66670	0.00000		0.83330	
Li8	0.33330		0.33330		0.83330	Li8	0.	.33330	0.33330		0.83330	
Li9	0.00000		0.66670		0.83330	Li9	0.	00000	0.66670		0.83330	
O1	0.00000		0.00000		0.25550	O1	0.	96150	0.01453		0.26145	
O2	0.66670		0.33330		0.25550	O2	0.	.65845	0.31601		0.26019	
O3	0.33330		0.66670		0.25550	O3	0.	36229	0.70117		0.24596	
O4	0.00000		0.00000		0.74450	O4	0.99797		0.99421		0.74000	
O5	0.66670		0.33330		0.74450	O5	0.	68881	0.39246		0.73410	
O6	0.33330		0.66670		0.74450	O6	0.	28437	0.70931		0.72025	
O7	0.33330		0.00000		0.92220	O7	0.	33112	0.98597		0.91790	
O8	0.00000		0.33330		0.92220	O8	0.	.02906	0.35033		0.90684	
O9	0.66670		0.66670		0.92220	O9	0.	.66398	0.66683		0.91660	
O10	0.33330		0.00000		0.41120	O10	0.	19836	0.04149		0.41708	
O11	0.00000		0.33330		0.41120	O11	0.	98020	0.32621		0.40265	
O12	0.66670		0.66670		0.41120	O12	0.	.67288	0.59355		0.41158	
O13	0.66670		0.00000		0.58880	O13	0.	67377	0.00719		0.57747	
O14	0.33330		0.33330		0.58880	O14	0.	.33601	0.35270		0.58834	
O15	0.00000		0.66670		0.58880	O15	0.96950		0.66023		0.58921	
O16	0.66670		0.00000		0.07780	O16	0.67161		0.00209		0.07621	
O17	0.33330		0.33330		0.07780	O17	0.33545		0.32744		0.07967	
O18	0.00000		0.66670		0.07780	O18	0.01599		0.68158		0.07096	
V1	0.03388		0.03388		0.00000	V1	0.04394		0.04151		0.99980	
V2	0.63282		0.33330		0.00000	V2	0.63925		0.3359	96	0.99933	
V3	0.33330		0.63282		0.00000	V3	0.34005		0.63412		0.00047	
V4	0.36883		0.03553		0.66670	V4	0.	.36707	0.0396	67	0.66643	
V5	0.	96447	0.3333	30	0.66670	V5 0.965		96578	0.3354	46	0.66462	
V6	0.66670		0.63117		0.66670	V6	0.66288		0.6323	31	0.66795	
V7	0.63018		0.96348		0.33330	V7	0.62676		0.965	10	0.33469	
V8	0.33330		0.36982		0.33330	V8	0.	.33274	0.3683	34	0.33377	
V9	0.03652		0.66670		0.33330	V9	0.	.03191	0.6633	35	0.33324	

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