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Understanding disorder in oxide-based electrode materials for rechargeable batteries

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Abstract

Most rechargeable ion batteries employ transition metal oxides or phosphates as the positive electrode. To facilitate facile migration of the active ions (e.g. Li- or Na-ions), which to some extent governs the battery functionality, the electrodes are typically composed of crystalline materials, wherein the ions are intercalated via well-defined migration pathways. However, the electrode materials are rarely perfectly crystalline and will inherently contain some disorder, which may originate from the material preparation process or be induced by the ion-intercalation process. In some electrode materials the electrochemical performance is damaged by disorder, whereas in other cases good performance is retained even after severe order–disorder transitions. This agrees with the emergence of several ab origine disordered or amorphous oxide-based electrodes with promising electrochemical performance. The term disorder is spanning a wide variety of deviations from an ideal crystal periodicity, from classical defects such as point defects, vacancies, stacking faults etc., to the amorphous state. Disorder, beyond classical defects, in battery electrodes has previously been largely overlooked, and we know little about the nature of the disorder and how it affects the battery performance. Developments in methods for characterisation of local atomic structures now allow us to gain detailed structural knowledge on the disordered part of the electrodes and studies within this field are emerging. This perspective provides a summary of the state-of-the-art within this field and the tendencies we are beginning to see outlined. These will be illustrated through selected examples. Finally, we discuss the key research questions within the field of disorder in electrode materials and the perspectives of answering these.

Development of improved rechargeable batteries is a major technological challenge for this century. Not only are batteries increasingly used in consumer products and electric vehicles, but the technology also constitutes a bottleneck in enabling renewable energy to replace fossil fuels in our electricity production [1–3]. To overcome this bottleneck, a long list of tasks lies ahead including developing sustainable and environmental-friendly battery chemistries, lowering production costs, enhancing power capabilities, prolonging the lifetime and improving the safety [4, 5]. Presently, multiple battery chemistries and technologies are being explored, such as lithium–air, lithium–sulfur, conversion type, all-solid state, various organic-based chemistries etc [6–12]. However, the intercalation-type Li-ion battery is still by far the commercially most utilised. As a natural extension of this technology, exchanging the active Li-ion by other more abundant elements such as Na, Mg, Al, Ca and Zn are being widely explored [13–16].

The intercalation-type rechargeable ion-battery is dependent on two types of functional materials: the electrodes and the electrolyte (figure 1). To function, the electrolyte must have a low electronic conductivity (not to short-circuit the cell) but a high ionic conductivity to transport the ions efficiently between the electrodes. The electrodes on the other hand must have both high electronic and ion conductivities for the electrons and ions to migrate efficiently in and out of the material. These properties need to be maintained during battery operation and alterations, which decreases the conductivities both at the surface or in the bulk, must be prevented as they will increase the internal resistance of the battery and decrease the practical capacity.
Traditional electrode materials for intercalation-type batteries are highly crystalline compounds with well-defined pathways for ion diffusion [4, 17]. On the anode side, graphite is the most widely utilised material for Li-ion batteries, but other materials are also increasingly being employed, e.g. Li$_4$Ti$_5$O$_12$ and silicon [18]. The cathode is typically composed of transition metal oxide or polyaniionic compounds. Above all others, three types of materials have been utilised commercially: phospho-olivines (e.g. LiFePO$_4$) [19–22], spinel-like metal oxides (e.g. LiMn$_{1.5}$Ni$_{0.5}$O$_4$, LiNi$_{x}$Mn$_{y}$Co$_{1-x-y}$O$_2$) [23, 24] and layered metal oxides with α-NaFeO$_2$ structure (e.g. LiCoO$_2$, Li[Ni$_{x}$Mn$_{y}$]$\alpha$-NaFeO$_2$) [3, 25–27]. The latter type constitutes >70% of the Li-ion battery market, while the other two more or less fill the remaining share [28]. These cathode materials are all based on cubic close packed oxygen lattices with the transition metals sitting in the octahedral sites and lithium ions in the tetrahedral (spinel) or octahedral sites (olivine and α-NaFeO$_2$). However, the cation-ordering differs, which mean that we are dealing with distinctively different structures with Li-migration taking place in one (olivine), two (α-NaFeO$_2$) and three (spinel) crystalline directions.

The fundamentals of the Li-ion migration mechanisms in these crystalline cathode materials are very similar (figure 2). In olivine and α-NaFeO$_2$-type materials, Li-ions migrate from one octahedral (LiO$_6$) site (o) to another via an activated tetrahedral (t) site as the direct migration through the edge shared between the two octahedra has too high energy to facilitate the migration [29–33]. The mechanism is denoted o-t-o migration. For the spinels, the concept is similar, but the migration path follows a t-o-t route [34]. For migration to be possible, the pathway must connect a series of possible Li-sites in such a manner that the path percolates the entire electrode particle. The electrostatic forces between the activated Li in the migration site and the transition metal, Li-ion or vacancy on the closest neighbouring sites is the main determining factor for the activation barrier of the migration process. The size of the barrier will depend on the transition metal valence, the combination of neighbouring species and the distance between the sites. Thus, the efficiency of the Li-migration is determined by the structure of the material. From these realisations a highly relevant question springs to mind: what if the electrodes are not perfectly crystalline?

1. Disorder in electrode materials—breaking the crystalline regime

It is well-known that materials with perfect crystallinity are difficult to obtained. This is especially true when materials are prepared industrially as powders of sub-micron crystallites. Furthermore, in rechargeable batteries ion intercalation and extraction can induce significant disorder or in some cases even amorphisation in crystalline electrode materials [35–37]. Here, we use the term disorder for structural distortions beyond defect chemistries in the classical sense such as point defects, vacancies, stacking faults, twin boundaries, etc. The structural nature and properties of electrode materials containing defects have previously been studied in great detail [38, 39]. Within this scope, the disordering process can lead to deterioration of the electrodes;
Figure 2. Illustration of the three categories of structural evolution during electrochemical cycling (i.e. charge or discharge) involving disorder: (a) *ab origine* disordered materials (i.e. materials prepared in a disordered state), (b) ion-intercalation or -extraction inducing irreversible disorder (e.g. cation disorder, nano-crystallisation, amorphisation etc), and (c) ion-intercalation or -extraction inducing reversible disorder by formation of disordered or amorphous intermediates.

However, the order–disorder transition can also lead to formation of materials delivering high and stable capacities (easily >200 mAh g\(^{-1}\)) \[40–49\]. Furthermore, electrode materials, which are *ab origine* disordered or amorphous (i.e. prepared in this state), can provide high and stable battery capacities and in some cases, they even outperform their crystalline counterparts \[50–56\]. This clearly reveals that it is possible to maintain a percolating and well-functioning pathway for ion-migration in spite of severe structural disorder.

Related to this, Gerbrand Ceders group at Berkeley University of California has provided an explanation for the high performance of cation-disordered rock salt structures. Using percolation theory \[57\], they showed, that despite the disordered cation lattice, \(o-t-o\) Li-migration through the structure is still possible \[58\]. However, whether the migration path is indeed open, depends to a large extent on the size of the tetrahedral site, which is governed by the composition and construction of the material. Based on these results, Lee *et al* wrote ‘…this ’ordering paradigm’ may have led the community to overlook a large class of cathode materials in which Li and TM share the same sublattice in a random (disordered) fashion…’ \[37\]. As underlined by this statement, these findings open for a new ground-breaking direction in the discovery of electrode materials with the percolation concept extending to structural disorder beyond occupational randomisation.

Unfortunately, our present knowledge about disordered or amorphous electrode materials does not go very far. Electrochemical properties of several disordered materials have been studied and observations of order–disorder phenomena have been reported but in many cases without providing any structural or mechanistic knowledge. Still, building on insights from recent research, it becomes clear that the phenomena of disorder in electrode materials can be divided into three categories (see figure 2):

(a) *Ab origine* disordered electrode materials, i.e. materials, which are disordered in their as-prepared state.
(b) Irreversible order–disorder transitions.
(c) Reversible order–disorder transitions.

Cases within these three categories will be described in the following. We note that the distinction between a disordered and an amorphous material is not clear-cut. The International Union of Crystallography (IUCr) states: ‘A material is a crystal if it has essentially a sharp diffraction pattern. The word essentially means that most of the intensity of the diffraction is concentrated in relatively sharp Bragg peaks.’ \[59\]. Thus, a material can be viewed as amorphous if it has no or only weak Bragg peaks. This definition will
be used herein. Materials denoted as disordered is thus regarded as partly crystalline and shows well-defined Bragg peaks.

1.1. Ab origine disordered electrode materials

Solid materials can naturally exhibit various degrees of disorder ranging from point defects, dislocations, stacking faults to bulk distortion and complete lack of long-range order. Within the frame of oxide-based battery electrodes, there are many examples of well-functioning ab origine disordered materials. In many of these cases, the disorder is comprised of cation disorder within an ordered oxygen framework e.g. in Li excess layered rock salts as Li$_{1.25}$Nb$_{0.25}$Mn$_3$O$_7$ [60], Li$_{1.2}$Mn$_{0.4}$Ti$_{0.6}$O$_2$ and Li$_{1.2}$Mn$_{0.4}$Zr$_{0.6}$O$_2$ [61] and Ni–Mn disorder in spinel LiNi$_{0.5}$Mn$_{1.5}$O$_4$ [62], and ‘complete’ disorder of cations including Li in cation disordered rock salts [63, 64]. Additionally, several cathode materials with significant bulk ab origine disorder or complete lack or long-range order have been revealed to exhibit reversible ion storage with promising capacities (see examples in Table 1). It is worth to note, that amorphous materials may hold advantages over their crystalline counterparts, as they may e.g. show reduced intercalation-stress in the structure, provide isotropic pathways for ion transport, and exhibit significantly smaller volume change during ion-intercalation/-extraction [48, 65–70]. Finally, amorphous materials hold a promise of reducing production costs as the crystallisation step, which normally requires high temperatures, may be omitted in the material synthesis [71].

Some of the most investigated oxide-based electrode materials are V$_2$O$_5$ [53, 56, 76–78], MnO$_2$ [69, 79–82] and FePO$_4$ [65, 66, 72], but others are also emerging like LiVO$_2$ [73], Nb$_2$O$_5$ [66] and V$_2$O$_5$–P$_2$O$_5$ [75]. Especially, amorphous V$_2$O$_5$ has recently received significant attention. Remarkably, amorphous V$_2$O$_5$ material can deliver capacities well above (>double) those of the crystalline counterpart [53]. Also, the capacity retention is better in the amorphous material.

Most of the amorphous electrode materials have not been studied in terms of the ion-storage mechanism or their atomic scale structure, but some examples of such studies do exist. E.g. Chae et al. [56] studied the structure of the amorphous V$_2$O$_5$ electrode (Figure 3) using a combination of extended x-ray absorption fine structure and ab initio molecular dynamics, and showed that the vacant sites for Li-ion storage are more accessible in the amorphous structure and can thus be populated to a higher degrees than in the crystalline counterpart. Furthermore, their results indicate that the structural changes during charge and discharge in the amorphous structure are smaller and the tendency of reversibility is higher than in the crystalline V$_2$O$_5$ material.

1.2. Irreversible order–disorder transitions

A classic example of irreversible disorder induced by ion-intercalation, i.e. an irreversible order–disorder transition, is the transformation of the layered α-NaFeO$_2$-type electrodes into cation-disordered rock salts upon repeated charge–discharge [35, 36, 67]. This was previously associated with capacity and voltage fade and deemed one of the primary problems for the α-NaFeO$_2$-type cathodes [27, 68]. However, it has since been discovered that Li$_x$M$_2$–O$_2$ rock salt structures with disordered cation lattices can exhibit high reversible storage capacities of >200 mAh g$^{-1}$ [49, 69]. Naturally, these discoveries have brought about a vast number of investigations of such materials in which the disorder originates from occupational disorder [27]. The same cannot be said for systems exhibiting more extensive disorder or amorphisation. Observations of loss of long-range order e.g. through loss of Bragg intensity in powder x-ray diffraction (PXRD) or by selected-area electron diffraction is by no means uncommon. A range of well-crystalline transition metal oxides have been reported to undergo irreversible disordering or in some cases complete amorphisation during ion-intercalation/-extraction. These count e.g. β-MnO$_2$ [69, 70], Li$_{2}$–VO$_3$ [71], Li$_{2}$MnO$_3$ [83], Ni$_{0.5}$TiPO$_4$ [84], and even nano-LiFePO$_4$ [85]. It is expected that many other materials could be added to this list.

Detailed structural studies of intercalation-induced irreversible order–disorder transitions have recently been carried out for rutile-like Li$_{x}$TiO$_2$ [46] and Li$_{x}$V$_2$O$_5$ [49] by operando x-ray total scattering and pair

| Amorphous electrode | Capacity/mAh g$^{-1}$ (active ion) | Reference |
|---------------------|-----------------------------------|-----------|
| V$_2$O$_5$          | >600 (Li), 240 (Na)               | [53, 56]  |
| MnO$_2$             | 210 (Li)                          | [69]      |
| FePO$_4$            | 140 (Li)                          | [72]      |
| LiVO$_2$            | 100 (Li)                          | [73]      |
| Nb$_2$O$_5$         | 75 (Li)                           | [74]      |
| V$_2$O$_5$–P$_2$O$_5$| 100 (Mg)                         | [75]      |
distribution function (PDF) analysis in combination with electron microscopy and electrochemical analysis. Both materials exhibit significant loss of long-range order during ion intercalation, however by comparing the systems it is evident that this is caused by quite different phenomena and that the ion-storage in the disordered state differ between the two cases. When the amount of lithium \(x\) in Li\(_x\)V\(_2\)O\(_5\) increases during battery discharge, Li\(_x\)V\(_2\)O\(_5\) transforms reconstructively from a layered structure into a single-phase disordered rock salt, \(\omega\)-Li\(_x\)V\(_2\)O\(_5\). At full-depths of discharge (i.e. insertion of 3Li) the domain size of \(\omega\)-Li\(_3\)V\(_2\)O\(_5\) is \(\sim 6\) nm with \(\sim 1.5\) nm sub-domains of dispersed cation-ordering. Rutile-like Li\(_x\)TiO\(_2\) on the other hand, transform during Li-insertion into \(\sim 5\) nm domains of a distorted layered \(\alpha\)-NaFeO\(_2\)-like phase (see figure 4). This transformation occurs through a translation along the \(c\)-axis of the Ti-atoms in every second [TiO\(_6\)] layer in rutile. Furthermore, in the discharged (Li-rich) state, amorphous grain boundaries of \(\sim 1\) nm thickness between the layered Li\(_x\)TiO\(_2\) domains are observed. The local structure of the grain boundaries can be described as an amorphous columbite-like Li\(_x\)TiO\(_2\) structure.

Interestingly, Li\(_x\)TiO\(_2\) and Li\(_x\)V\(_2\)O\(_5\) delivers stable capacities of \(\sim 200\) and \(310\) mAh g\(^{-1}\) in their disordered state, respectively. Thus, it is also of high interest to investigate the structural transitions during charge–discharge in the disordered material. In the disordered rock salt \(\omega\)-Li\(_3\)V\(_2\)O\(_5\), Li-ion insertion and extraction cause a two-phase transition between \(\omega\)-Li\(_3\)V\(_2\)O\(_5\) and an amorphous \(\beta\)-Li\(_{0.3}\)V\(_2\)O\(_5\)-like structure with a domain size of just 1.5 nm. The \(\beta\)-Li\(_{0.3}\)V\(_2\)O\(_5\)-like structure is built from a rock salt-like and a V\(_2\)O\(_5\)-like part. Hence, it can be considered an amorphous hybrid between the \(\omega\)-Li\(_3\)V\(_2\)O\(_5\) and \(\beta\)-Li\(_{0.3}\)V\(_2\)O\(_5\) end-members. In contrast, the disordered layered Li\(_x\)TiO\(_2\) undergoes charge and discharge via a complete solid-solution reaction. Hence, the comparison between the findings in these studies underlines the variety in both disorder phenomena, i.e. bulk disorder and nano-crystallisation, and in ion-storage mechanisms in disordered materials, i.e. two-phase transition versus solid solution reaction.

### 1.3. Reversible order–disorder transitions

For some electrode materials, reversible formation of disordered phases are observed during battery charge or discharge. The reversibility refers to the fact that in these cases, disorder is induced at some point during either ion-intercalation or -extraction, but crystallinity is regained at a later stage in the electrochemical cycle. The phenomenon is typically observed as intermediate loss of Bragg intensity in diffraction experiments, but in many cases the observation is noted but not explained further in a structural context. Such observations have been made e.g. for Li\(_3\)V\(_2\)(PO\(_4\))\(_3\) [86, 87] and LiFePO\(_4\) [88].

Interestingly, the disordered phase can form either as an end-member in the charge or discharge process (i.e. at high or low states-of-charge) or it can form as an intermediate in the charge or discharge process (i.e. at intermediate states-of-charge).

An example of a reversible order–disorder transition with formation of an amorphous phase at intermediate states-of-charge is found in olivine NaFePO\(_4\) during Na-ion intercalation and extraction [89].
Figure 4. During Li-intercalation (i.e. discharge) in rutile Li$_x$TiO$_2$ an irreversible order–disorder transition occurs wherein the rutile structure transforms to ca. 5 nm domains of layered α-NaFeO$_2$-type Li$_x$TiO$_2$ separated by thin (<1 nm) grain boundaries with a disordered columbite-like structure. Reproduced from [46] with permission of The Royal Society of Chemistry.

Herein, charge and discharge leads to a loss of >50% of the total diffracted x-ray intensity in an operando PXRD experiment. Studying the local structure of the electrode at intermediate states-of-charge and—discharge using PDF analysis revealed formation of an amorphous Na$_x$FePO$_4$ phase, which constitutes up to 39 mol% of the active material. The local structure of the amorphous Na$_x$FePO$_4$ intermediate is olivine-like with a lattice that matches that of the Na-rich NaFePO$_4$ in two dimensions and the Na-poor FePO$_4$ in the last dimension. The local olivine-like order in the intermediate phase only extents to 1.1 nm. This corresponds to 1–2 unit cells of the crystalline NaFePO$_4$ olivine structure. The amorphous intermediate is considered to relieve the large misfit strain (12 vol%) at the grain boundary between the coexisting Na-rich and Na-poor phases at intermediate states of charge. Noticeable at the end-of-charge and—discharge the electrode regains >80% of the crystallinity.

A reversible order–disorder transition has also recently been reported for Lipscombite Fe$_{2-y}$(PO$_4$)(OH)$_3$3y(H$_2$O)$_{3y-2}$ [90]. As Na-ions are inserted into the material, a Na$_x$Fe$_{2-y}$(PO$_4$)(OH)$_3$3y(H$_2$O)$_{3y-2}$ solid solution forms, however as xNa increases, the crystalline solid solution transforms into an amorphous phase (figure 5). The fraction of the amorphous phase increases with continued Na-insertion, i.e. the amorphous phase is a Na-rich end-member. Through PDF analysis the local atomic structure of the amorphous phase is found to resemble the crystalline Na$_x$Fe$_{2-y}$(PO$_4$)(OH)$_3$3y(H$_2$O)$_{3y-2}$ structure, however the structural order only extents to ca. 6 Å, i.e. this phase is truly amorphous with only very local structural order.

2. Future perspectives

Previous studies of disordered electrode materials have mainly focused on capacity- or rate-improving efforts, while structural characterisation in many cases have been limited to the crystalline part of the materials. Thus, presently we only have a vague structural understanding of disorder in battery electrodes and of how ion-storage mechanically occurs in disordered materials. Whether we aim to hamper performance-damaging disorder or utilise disorder to our advantage, we need to build an understanding of disorder in electrode materials.

Elucidating the atomic-scale structure of the disordered part of an electrode is naturally important when considering the importance of the ion migration pathway for the battery performance. If the ions must migrate through a disordered phase, we need to understand how the disordered structure facilitates the ion-migration. This further raises the point, that we also need to understand the relative arrangement of the disordered and crystalline parts of the electrode on the nano- or micro-scale, i.e. is disorder resulting from framework distortions, grain-boundary formation, nano-crystallisation or bulk disorder/amorphisation? This will obviously affect the intercalation process as the extent to which the ions are required to migrate through the disordered structure will vary through these cases. Furthermore, as the examples above illustrate, some materials undergo severe disordering during ion-intercalation and -extraction. Firstly, the mechanisms for the order–disorder transitions are not resolved. Secondly, it is an unsolved puzzle why ion-intercalation induces disorder in some materials, while others appear to remain perfectly crystalline.

Progress in techniques capable of probing non crystalline local atomic structures has opened new doors for studies of disordered electrode materials, as illustrated by the examples described above. The techniques
count e.g. high-resolution transmission electron microscopy, solid state nuclear magnetic resonance spectroscopy, extended x-ray absorption fine structure spectroscopy and total x-ray scattering with PDF analysis. Obviously, these tools allow for detailed studies of disordered or even amorphous atomic structures. These types of studies might be used as starting point for further investigations of ion migration pathways using molecular dynamics simulations, void space analysis etc, and the findings could be linked to electrochemical investigations of the transport properties using e.g. impedance spectroscopy or various intermittent titration techniques. Furthermore, several of the structural characterisation techniques can be carried out under dynamic or operando conditions, which allows order–disorder transitions to be studied ‘live’ as they occur during battery charge and discharge. This is a powerful multimodal approach, which provides a direct link between the structural evolution and the electrochemical properties.

The hope is naturally, that by increasing our material specific knowledge on structural disorder and order–disorder transitions in battery electrodes, we can with time elucidate general correlations between the characteristics of the material, the nature of the disorder and the electrochemical performance. This will aid in the development of novel battery material design descriptors for the future generations of efficient, cheap and sustainable batteries.

Data availability statement

No new data were created or analysed in this study.

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