

Original citation:

Coppo, Paolo. (2017) Lithium ion battery cathode materials as a case study to support the teaching of ionic solids. Journal of Chemical Education.

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Lithium ion battery cathode materials as a case study to support the teaching of ionic solids

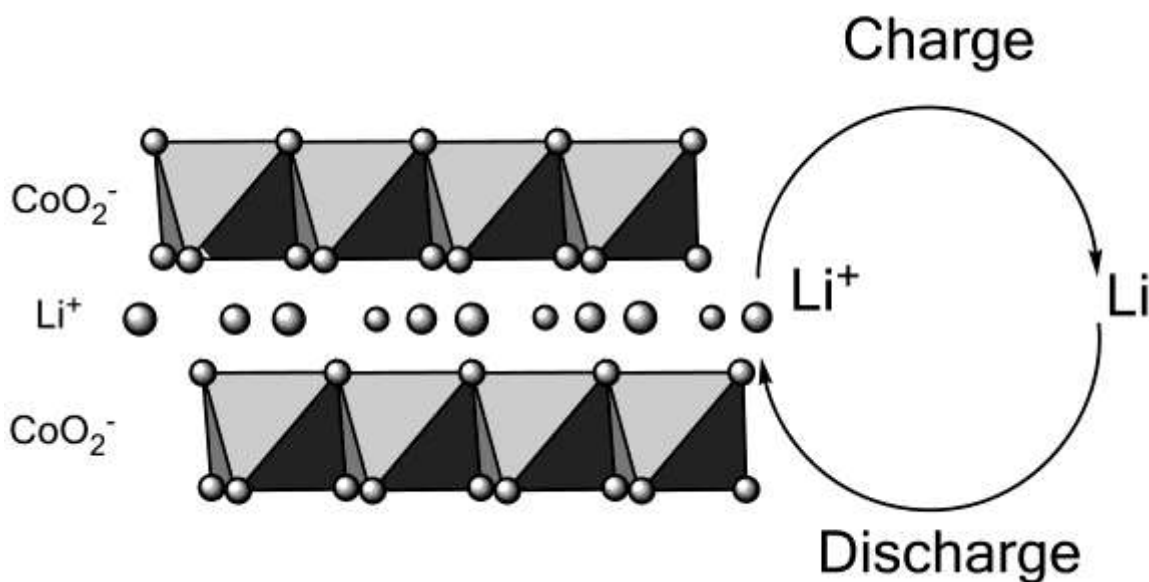
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ABSTRACT

A lithium ion battery cathode material is proposed as a case study to investigate ionic solids in an undergraduate inorganic chemistry course. The concepts of unit cell, ionic lattice arrangements, non-stoichiometric compounds and the
10 thermodynamics of defects in crystals are introduced to students within the framework of research into materials for rechargeable batteries.

ABSTRACT GRAPHIC



KEYWORDS

15 Inorganic Chemistry, Inquiry-Based/Discovery Learning, First Year
Undergraduate/General, Problem Solving/Decision Making,

INTRODUCTION

20 Teaching science by case study and class problem solving has seen an increase in popularity over the past twenty years, as a more effective way of transferring knowledge over the traditional lecture.¹⁻⁸

The study of solid state is generally integrated in undergraduate inorganic chemistry modules at University level, often linked to topics like transition metal
25 chemistry and atomic bonding. Undergraduate lab experiments in inorganic chemistry often focus on the solution chemistry of transition metal complexes and solids are generally overlooked, with only few practical experiments reported.⁹⁻¹¹ Yet, understanding the structure of inorganic solids is becoming increasingly relevant for a chemist, as new materials, such as hybrid perovskite have shown
30 extraordinary performance in dye sensitized solar cells.¹² As well as energy harvesting devices, rechargeable lithium ion batteries have revolutionized the world of electronics: access to light, compact and relatively large-charge storage units, capable of powering full color displays for several hours has provided a boost to the capability of portable devices such as smart phones, tablets and laptops.¹³⁻¹⁴ The
35 operating principles of a lithium ion battery have entered the undergraduate chemistry curriculum and have recently even been featured at high school level in the United Kingdom.¹⁵ A comprehensive discussion of the electrochemistry of Li ion batteries for the purpose of chemical education was reported by R. S. Treptow in 2003.¹⁶

Such devices rely on the migration of Li^+ ions from the cathode to the anode during charge and the reverse during discharge, when in use. The anode is typically a layered carbon structure which can accommodate Li atoms by intercalation, whereas the cathode is generally an ionic solid comprising a transition metal ion for redox purposes and a crystal structure that allows the Li^+ ions to migrate in and out of it. As such, the cathode is an ideal framework to introduce undergraduate students in inorganic chemistry to the concepts of unit cell and crystal lattice of ionic solids, as well as providing an insight in the relevance of inter-ionic arrangements in different classes of crystals. In addition, the concept of defects in the lattice and that of non-stoichiometric compounds are in essence two ways of looking at the same phenomenon and the former can provide a practical insight into the thermodynamics of crystals and help understanding the decline in performance of batteries over time.¹⁷

LEARNING OUTCOMES

In this article, the aim is to provide educators with a platform to link theoretical concepts with practical applications which are very relevant to everyday students' life. Using LiCoO_2 as a case study material, it is possible to introduce the core concepts of a solid state course. Using calculations and observations on this case study material, students should learn to:

- Appreciate that ions are shared among cells and calculate how many ions (or atoms) are contained in the unit cell and hence derive the compound formula.
- Calculate how many ions of a given type are present in a given mass unit of the compound, hence reinforcing the concept of mole.

-
- Appreciate that the unit cell is a self-contained representation of the material and therefore calculating the density of a unit cell using the cell parameters leads to the density of the bulk material.
 - Calculate the distance between ions in a crystal, using the properties of triangles and the geometry of solids.
 - Appreciate the importance of defects in crystals and that of transitions between different crystal structures in a compound.

THE UNIT CELL

While understanding the fundamentals of a simple rocksalt unit cell appears trivial, students often find ternary ionic structures AB_mX_n significantly more complicated. In such structures, the bonding between anions and cations might have different ratios, leading to tetrahedral, octahedral or more complex coordination arrangements, but the overall stoichiometry of the unit cell always represents an integer multiplier of that of the bulk solid. Projection representations, such as the horizontal sections depicted in figure 1, are a preferable way to represent a unit cell, over tridimensional sketches. The latter allow to get a grasp of the overall shape and composition of the cell and allow to appreciate the layered structure, but for educational purpose, they lack rigor. From a projection, students can independently confirm the proportions between ions and the chemical formula of a ternary compound, by adding the individual fractional contributions of each ion in the cell. Corner ions are shared among eight cells, edge ions are shared among four cells, face ions are shared between two cells, while internal ions are not shared and belong fully to the cell. Figure 1 shows the unit cell of a ternary ionic compound of lithium, cobalt and oxide ions, with its thirteen vertical sections,

named using fractions between 0 and 1. It is possible to count three lithium ions (two are inside the cell at 2/12 and 10/12 and one is made out of four edge ions at 6/12), three cobalt ions (two are inside the cell at 4/12 and 8/12 and one is made out of eight corners at 0 and 1) and six oxide ions (four are inside the cell at 1/12, 5/12, 7/12 and 11/12; two are made out of eight edges at 3/12 and 9/12). Overall, the cell contains three units of a compound with formula LiCoO_2

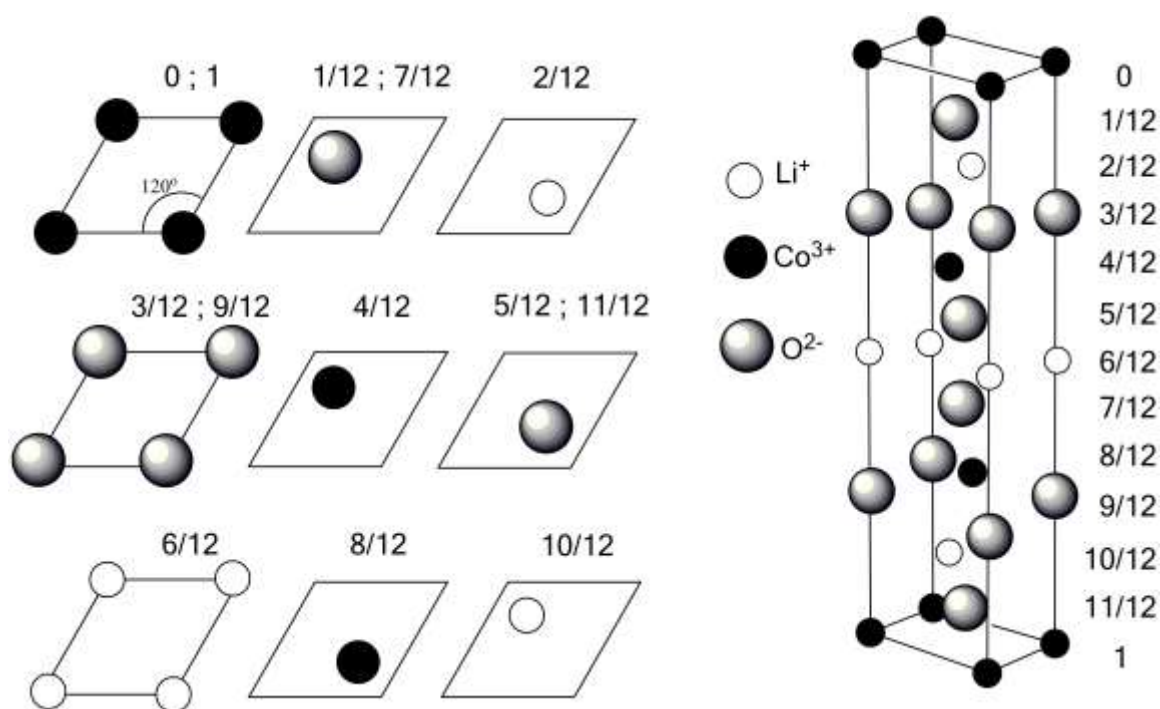


Figure 1: projections and 3D representations of the LiCoO_2 rhombohedral crystal cell. The unit cell contains three units formula of the compound.

From the chemical formula, it is interesting and relatively straightforward to calculate the theoretical charge capacity of a given material in a lithium ion battery. Specific charge capacity is measured by the industry in Ampere-hour per gram (Ah

g⁻¹). Given one Ampere-hour is by definition the charge transferred by a one Ampere current over one hour, hence 3600 Coulomb (C), the problem to work out is the number of charge carriers (lithium ions) per gram of compound for the structure of LiCoO₂ depicted in figure 1. Students should be able to perform such calculations independently, by dividing the Avogadro's constant ($N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$) by the formula weight ($FW = 97.87 \text{ g mol}^{-1}$). Multiplying the resulting number of Li⁺ ions by the elemental charge ($C = 1.6 \times 10^{-19} \text{ C}$) leads directly to the theoretical charge capacity as 982.8 C g⁻¹, or, as above, 0.273 Ah g⁻¹ (see equation 1).

$$\text{Charge capacity} = \frac{n\text{Li}^+ N_A C}{FW}$$

Equation 1.

This simple problem solving exercise engages the students in a real world application of chemical calculations involving moles and molar mass, which for once go beyond the “how many grams in a mole” scenario. At the same time, the projection representation provides a practical way for students to understand the fundamentals of complex unit cells, which 3D representations fall short of describing. Students’ understanding can be probed on why low atomic weight lithium is the preferred charge carrier and how to produce a material with a higher charge capacity: reducing the formula weight, results in a higher number of Li⁺ ions per gram of cathode.

All lithium ion batteries on the market display the charge capacity in Ah and students can calculate how many grams of the cathode material are necessary to

make up the battery of their smartphone or tablet device. As discussed later in this article, theoretical charge capacity is an over-estimation, but nonetheless these calculations have some value in comparing the relative performance of different materials.

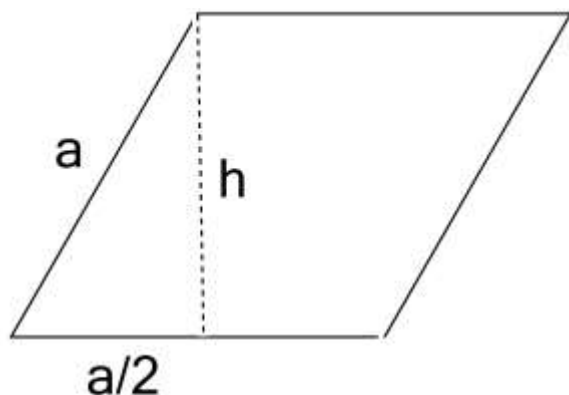
Density (ρ) calculations can be performed for any crystalline material, by knowing the cell parameters and the number of unit formulas (Z) contained in the cell, using the following equation, where F_w is the formula weight, N_A is Avogadro's constant and V is the volume of the unit cell, as shown in equation 2.

$$\rho = \frac{F_w Z}{N_A V}$$

Equation 2.

It is worth stressing that the numerator in the fraction is the formula weight of the ions in the cell in g mol^{-1} and therefore the denominator needs to contain the Avogadro's constant to convert it into the actual mass of ions in the cell. In the case of LiCoO_2 , as depicted in figure 1, given $Z = 3$ and the parameters of the rhombohedral unit cell, as measured by x-ray powder diffraction are $a = b = 281.4$ pm (sides of the rhomboid); $c = 1405.2$ pm (vertical height of the cell). Given the angles are 60° and 120° for the rhomboid and 90° for the vertical face, the volume of the cell can be calculated as shown in figure 2 ($V = 96.36 \times 10^{-24} \text{ cm}^3$) and the density can be calculated as 5.06 g cm^{-3} .¹⁸ Such calculations rely on students

recalling the properties of right angle triangles and how to work out the volume of simple solids.



$$h = \left(a^2 - a/2^2\right)^{1/2}$$

$$V = a \times h \times c$$

$$\rho = \frac{3 \times 97.87 \text{ g mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1} \times 96.36 \times 10^{-24} \text{ cm}^3} = 5.06 \text{ g cm}^{-3}$$

145 *Figure 2. Calculations to work out the density of LiCoO₂ solid.*

LiCoO₂ from crystallographic data appears as a sequence of layers that follow the motif Co/O/Li/O, where the first layer has a quasi-close packed configuration of the ions. The second layer has the same configuration but it is displaced so that
 150 each ion sits on top of the dips marked as *b* in figure 3. The third layer also has the same configuration, but the ions sit on top of the dips marked as *c*. The fourth layer sits exactly on top of the first and overall the repeating pattern is an ABC type, as shown in figure 3. The Co/O/Li/O motif and the repeating pattern combine to give twelve possible combinations, which correspond to the different layers in the unit
 155 cell, bearing in mind the top and the bottom layers in the cell only count as half layers, as are shared between two adjacent cells.

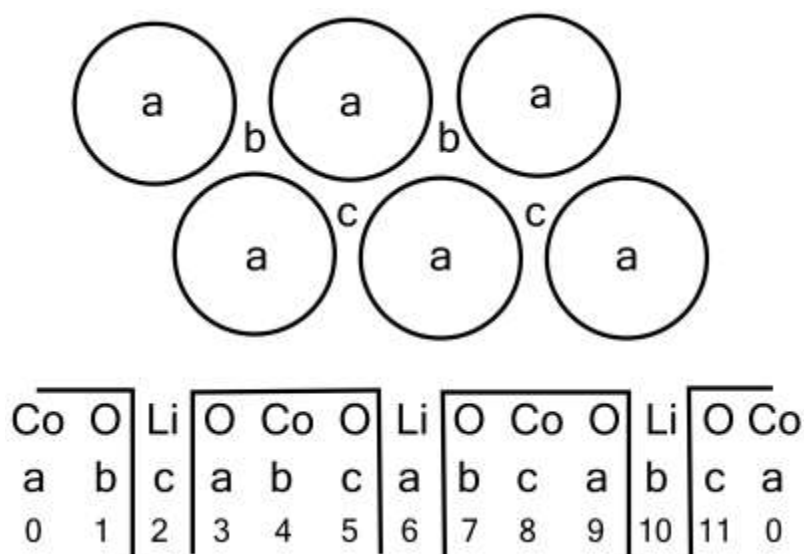


Figure 3. Layers of ions in the crystal lattice.

The layered structure of LiCoO_2 lattice can also be viewed as alternated layers of CoO_2^- , with an octahedral arrangement of oxide ions around Co^{3+} and layers of Li^+ ions, which can be extracted from the crystal in the presence of a suitable voltage. In a perfect octahedron, the distance between the six vertices is the same and in our case it corresponds to the lattice parameter a . The ion at the center is equidistant to all six vertices. Students should then be able to compute the distance between Co^{3+} and O^{2-} in LiCoO_2 .

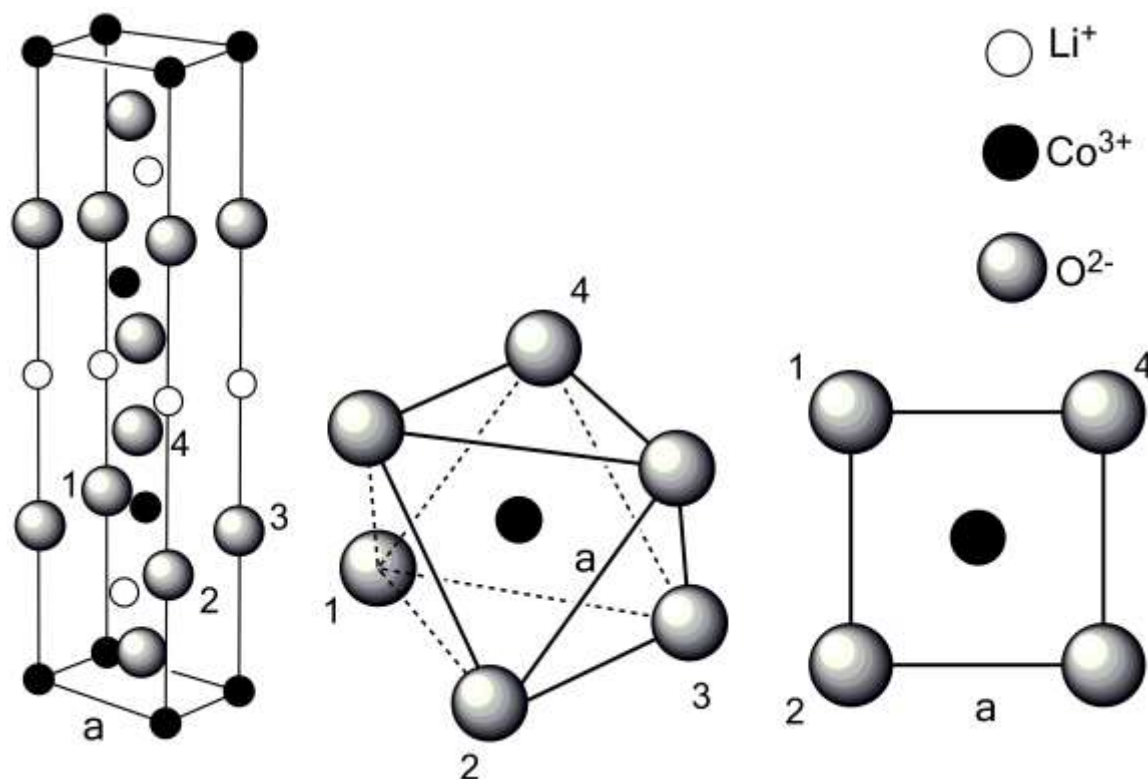


Figure 4. Octahedral arrangement of oxide ions around the Co^{3+} ion and section of the equatorial plane of the octahedron.

Knowing the distance between two oxide ions in the octahedron equals the
 170 lattice parameter $a = 281.4 \text{ pm}$, the distance between Co^{3+} and O^{2-} in the layer can
 be calculated as $\frac{a\sqrt{2}}{2}$, which gives 198.98 pm (see figure 4). This result is in
 excellent agreement with the sum of the ionic radii of O^{2-} (140 pm) and Co^{3+} (60 pm).

DEFECTS AND NON STOICHIOMETRIC COMPOUNDS

175 During charging, in the presence of a voltage exceeding the potential of the cell,
 ions are depleted from the cathode crystal structure, resulting in the formation of

the non-stoichiometric compound Li_xCoO_2 , where $0 < x < 1$. The proportion of cobalt +3 and +4 ions changes continuously to maintain charge neutrality. Ion depletion is an endothermic process, as energy is required to break the lattice and free the ions from the crystal. Ion depletion from the cathode also results in vacancies in the crystal structure, which are typically referred to as Schottky defects. A small number of defects in a crystal promote stability by increasing the entropy of the system, which accounts for defects existing as the norm in any crystal. As the number of vacancies increases, the endothermic contribution required to disrupt the lattice overwhelms the entropic advantages and overall the Gibbs energy of the crystal increases, rendering the structure less stable.

When $x = 0.5$ in Li_xCoO_2 , the compound reaches a new stoichiometry and the formula can be rewritten as LiCo_2O_4 , which belongs to the spinel class of materials and could rearrange in the stable cubic cell, which comprises 8 lithium ions (8 corners counting for one ion and 6 ions on the faces counting for 3), 16 cobalt ions of mixed +3/+4 oxidation states (all internal to the cell) and 32 oxide ions (all internal to the cell), as depicted in figure 5.¹⁹

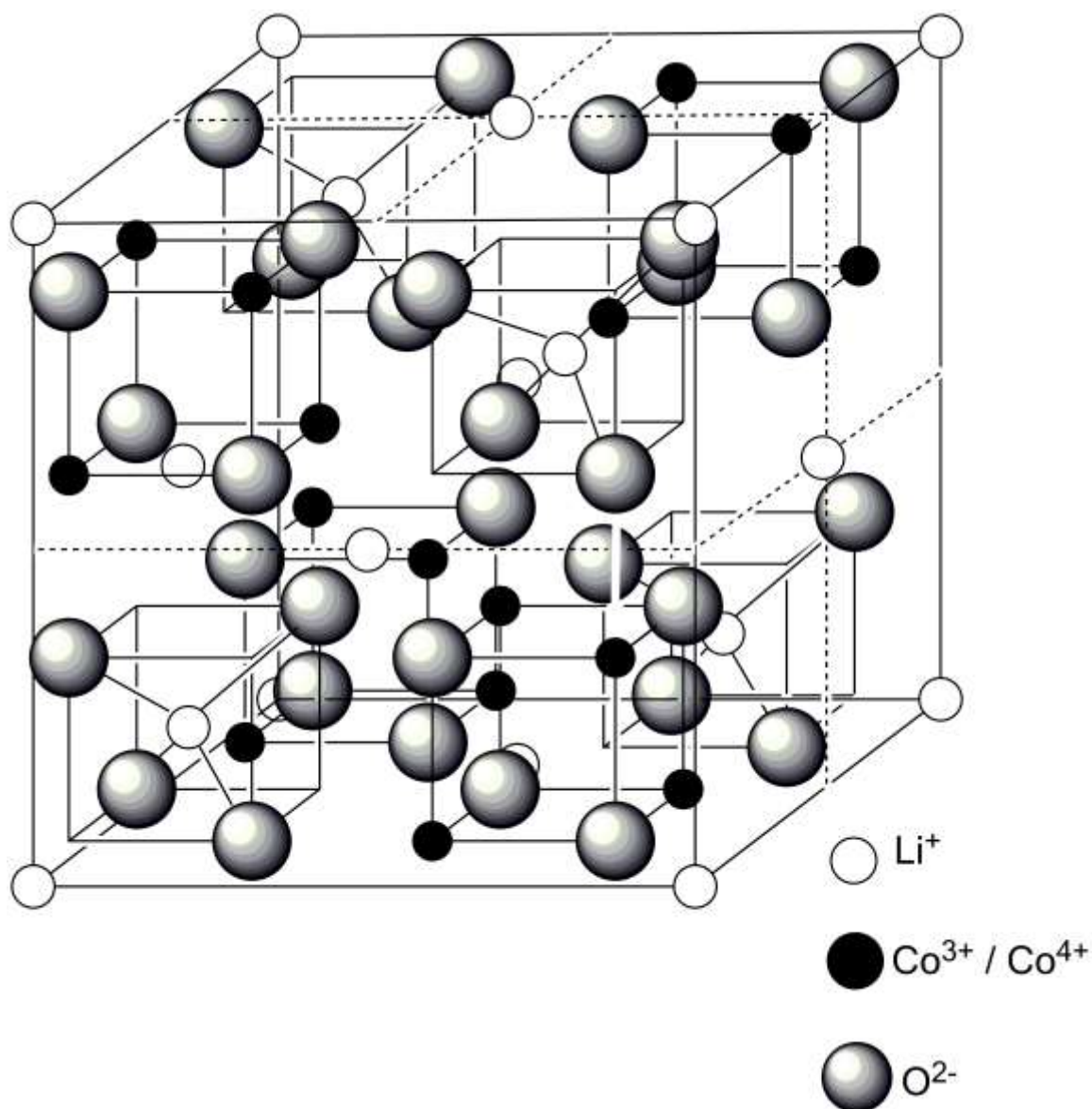


Figure 5. Crystal structure of a LiCo_2O_4 spinel, retaining the layered structure of O^{2-} ions, which is visible along the diagonal of the cube.

Bearing in mind the layered arrangement of oxide ions in the original structure and looking at how the oxides and the cobalt ions in the spinel are still arranged in diagonal layers, the phase transition mainly involves a rearrangement of the lithium ions, made simpler by the large number of vacant sites. If the ion depletion was to

continue until $x = 0$, the cathode would transform into the stoichiometric compound CoO_2 , which is known to be unstable.

Crystal rearrangements need to be avoided during battery life and therefore the theoretical charge capacity calculated initially is a figure that can never be reached. The best LiCoO_2 cathodes operate at a capacity of ca. 0.130 Ah g^{-1} , which is less than 50% of the theoretical capacity calculated, or in other words less than half of the potential charge carriers can be depleted from the crystal during charge. Charge/discharge cycles performed at or close to the charge capacity of the unit result in diminished battery life, as permanent damage to the layered crystal structure occur more frequently the more the crystal is depleted of Li^+ ions.

Typically the charging voltage is controlled to avoid excessive depletion.

Other cathode materials such as LiFePO_4 and LiMn_2O_4 have a considerably more complicated unit cell (olivine and spinel respectively) and the analysis of those is far too advanced for an introduction to ionic solids. Perovskite type materials have gained considerable interest in the field of dye sensitized solar cells and the basic unit cell of an ABX_3 structure is suitable to perform calculations to work out the number of ions in the cell and the density of the material.²⁰ In addition, ionic distances can be calculated, knowing the size of the unit cell, as described in the supplementary material.

METHOD, STUDENT FEEDBACK AND RESULTS

The approach presented in this article was implemented as part of an introduction to Inorganic Chemistry module for first year students of Chemistry at The University of Warwick. The “case study” approach was used to teach the properties of the unit cell, ionic solid lattices, thermodynamics and defects in ionic

solids. Lectures were interactive: students were asked to join in small groups of two

225 or three and try to work out the ion count in the cell, the charge capacity of the material and the density of the material, knowing only the basic definitions.

Typically, students showed an excellent level of engagement in the class and managed to partially and occasionally completely solve the problems within the small group. Methods and calculations were then discussed together, with the help
230 of the teacher. Anonymous feedback was collected at the end of the series of ten lectures from 26 students. The brief feedback form consisted of three statements based on a Likert-type scale:

a) The module based on LiCoO_2 makes the topics more interesting

b) The use of LiCoO_2 as a “case study” makes concepts easier to understand

235 c) I would like a “case study” approach implemented in other modules

The students' answers are summarized in table 1.

Response Distribution by Agreement/Disagreement <i>N</i> = 26					
Statements for Response	Strongly Disagree	Disagree	Neither Agree nor Disagree	Agree	Strongly Agree
The module based on LiCoO_2 makes the topics more interesting	0	0	0	13	13
The use of LiCoO_2 as a “case study” makes concepts easier to understand	0	1	3	13	9
I would like a “case study” approach implemented in other modules	0	0	1	13	12

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Table 1. Comparison of feedback from Students.

240

All students agreed for their feedback to be used for the purpose of research in education. The feedback collected is overwhelmingly positive: 100% of students agree the case study approach used makes the topic of solid state structure more interesting, which was the first objective, when the module was designed.

245

96% of students would like to see a similar approach implemented in other year one modules. Even more importantly, 84% of students agree the case study approach helps understanding concepts. Students were also given the opportunity to comment on the approach, some selected comments from students involved in the module are reported below.

250

“Great, as long as there is still variety with use of other examples.”

“It was very useful to stick to LiCoO_2 as it allowed me to learn about the different aspects of a crystal using a familiar structure + made it more interesting.”

255

“The use of examples/case studies etc. makes it easier for me to see what is going on and how to apply the concepts with the example.”

“Great to learn about real life applications. Very interesting!”

260 *“I think seeing LiCoO₂ keep coming up made the idea of solid state less daunting,
made it more relevant.”*

*“Would be interesting to have an inefficient battery example to compare LiCoO₂
to.”*

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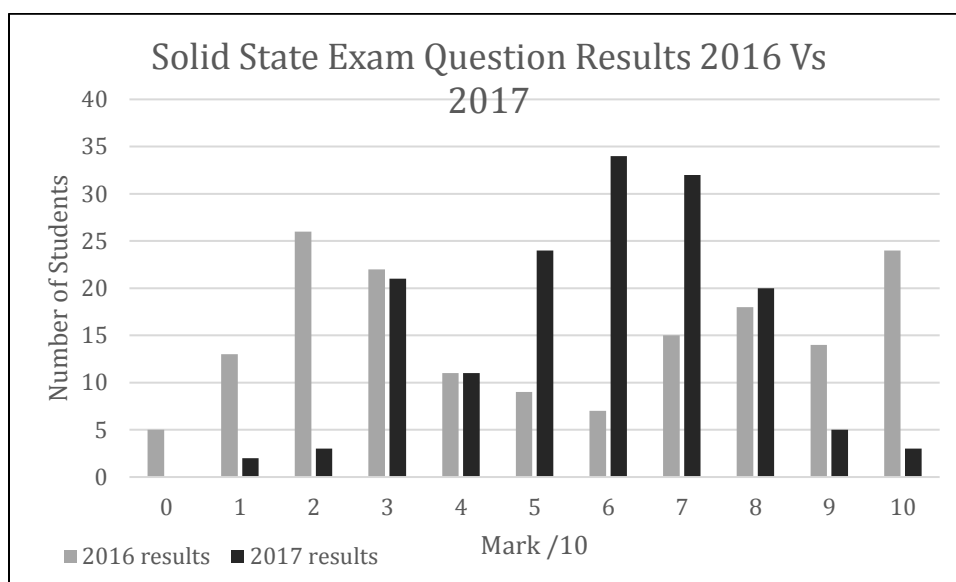
The solid state component of the first year Inorganic Chemistry module at Warwick aims to enable students to understand the different arrangements of atoms and ions in a crystal, to work out the composition of the unit cell, atomic and ionic distances and therefore properties of the bulk material, such as density.

270 In addition, it aims to enable them to understand the basic thermodynamics of perfect and non-perfect lattices. This ten lectures component of the module is assessed via exam only and the 45 minutes exam question is designed to probe students' understanding and their ability to perform such calculations. In 2016, the material was delivered following the textbook structure and LiCoO₂ was only

275 used as an example of a ternary ionic structure.²¹ In 2017, the material was delivered using the case study approach described in this article throughout the lectures. The exam results (see graph 1) based on similar student populations show a non-normal distribution of marks between 0 and 10 for the 2016 class (164 students), with an average mark of 5.42/10. The 2017 class (155 students)

280 obtained a higher average mark of 6.04/10, an increase of 11.4%. The distribution of marks for the 2017 class was closer to a bell shaped curve. While

it is difficult to comment on the very different distribution of marks for the two classes, it appears the case study approach is an improvement over the previously adopted, textbook-like delivery of the material. Looking through the answers students gave, it was very encouraging to see how the vast majority of them understood the concept of unit cell, how to work out the number of ions and therefore the unit formula, whereas a significant number of students of the previous class (2016) struggled with these very basic concepts.



Graph 1.

CONCLUSIONS

In conclusion, ternary ionic solids such as LiCoO_2 , widely used as cathode materials in rechargeable batteries, are an ideal case study for students to develop a cause-effect understanding of the properties of a material, as a function of its solid state structure. Many of the issues related to Li^+ ion batteries can be traced to the solid state structure of their components. This approach is aimed at stimulating

students' interest towards a topic typically seen as abstract and somewhat less important, as rarely solid state features in undergraduate lab experiments.

Feedback from students, as well as exam results suggest the method delivers on the desired learning outcomes.

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ACKNOWLEDGMENTS

The University of Warwick is gratefully acknowledged for funding this work. Prof. R. I. Walton and Dr. J. P. Rourke are gratefully acknowledged for insightful discussions. Mrs K. Yeandle-Hignell is acknowledged for helping to produce the figures.

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