Mechanochemical Reduction and Doping of Cobalt (II,III) Oxide (Co$_3$O$_4$) by Lithium Metal: A Facile Route to Li$_x$Co$_y$O Materials

Nathan Davison$^a$, Isabel Arce-Garcia$^b$, Jamie A. Gould$^{*b}$, James A. Dawson$^{*a,d}$, Erli Lu$^a$

$^a$Chemistry – School of Natural and Environmental Sciences, Newcastle University, Newcastle upon Tyne, UK
$^b$Faculty of Sciences, Agriculture and Engineering, Newcastle University, Newcastle upon Tyne, UK
$^c$School of Engineering, Newcastle University, Newcastle upon Tyne, UK
$^d$Centre for Energy, Newcastle University, Newcastle upon Tyne, UK

KEYWORDS: Mechanochemistry, Lithium, Cobalt Oxide, Doping, Reduction, Li-ion Batteries, Cathode Materials

ABSTRACT: The reduction and doping of transition-metal oxides (MO$_x$) are essential processes in battery materials manufacturing, heterogeneous catalysis and metallurgy. However, due to the stability and inertness of MO$_x$, their reduction and doping are energetically demanding, requiring high temperature and/or a strong electro-potential. In this work, by introducing lithium metal as both a reductant and Li-ion source, we report the facile (10–15 minutes at room temperature) reduction and doping of cobalt (II,III) oxide (Co$_3$O$_4$) under mechanochemical conditions, to produce lithium-doped cobalt oxides (Li$_x$Co$_y$O) and cobalt metal. Reactions at different stoichiometric ratios are studied in one-pot and stepwise manners. Our combined experimental–computational analysis reveals the strongly exothermic profile of these reactions and proves that higher lithium contents in Li$_x$Co$_y$O materials are achievable by conducting the reaction in a stepwise manner. This work provides a facile route for the reduction of Co$_3$O$_4$ and its Li doping to producing Li$_x$Co$_y$O and LiCoO$_2$ battery cathode materials, which can only currently be made under energy- and carbon-intensive conditions (high temperatures for several hours).

Transition-metal oxides (MO$_x$) play essential roles in materials science and catalysis. Reduction and doping are two crucial processes to enable and improve the performance of MO$_x$-based materials and catalysts. Therefore, enormous research effort has been invested into these fields, from the chemical research communities [1] and beyond [2]. However, MO$_x$ materials feature thermodynamically stable lattice structures, rendering their reduction and doping processes energetically demanding and with harsh conditions required.

For example, cobalt (II,III) oxide (Co$_3$O$_4$) is widely applied in Li-ion battery (LIB) materials [3], catalysis [4] and gas sensors [5]. In LIB research, Co$_3$O$_4$ serves as an anode material, as well as a starting material to manufacture one of the most important LIB cathode materials: lithium cobalt oxide (LiCoO$_2$, LCO) [6]. Co$_3$O$_4$ is also an important source of Co metal through its reduction by the aluminothermic reaction or with carbon in a blast furnace [7]. In these applications, reduction and doping (e.g., Li$^+$ doping) play crucial and irreplaceable roles [8]. However, Li$^+$ doping of Co$_3$O$_4$ only occurs at $>600 \, ^\circ C$ over a duration of hours [6]. Comparably, the reduction of Co$_3$O$_4$ to Co metal [7] also only occurs under extreme conditions, such as under reducing atmosphere (hydrogen/methane/ethanol) at 800–1100 $\, ^\circ C$ [9,10], with hydrogen plasma at $>800 \, K$ [11], or at the nano-scale under strongly electrochemical reduction conditions [12]. Facile (room temperature and short reaction times) Co$_3$O$_4$ reduction and Li$^+$ doping at preparative scales are highly desirable, as they could potentially pave the way for new low-carbon and sustainable routes toward LIB materials (e.g., LCO) and Co metal. However, to the best of our knowledge, such facile Co$_3$O$_4$ reduction and doping reactions are currently unknown.

Mechanochemistry exploits mechanical forces (impact, shearing and pressing) to directly promote chemical transformations [13]. Compared to conventional solution-phase (stirring and heating) and solid-phase (high-temperature calcination) chemical synthetic methods, mechanochemistry features solvent-free and energy efficacy advantages. Mechanochemistry has a long history [14], with humans unintentionally using grinding to deliver chemistry in the prehistoric ages. This research field had been in hibernation until the 2000s, but the last two decades have witnessed a renaissance and upsurge in mechanochemistry research, driven mainly by the demands for low-carbon, sustainable and energy-efficient chemical synthesis methods [15]. Since then, mechanochemical methods have been used for organic [16], inorganic/organometallic [17], polymer [18] and supramolecular [19] chemistry. With regards to materials science, mechanochemical methods have also been employed to synthesize metal oxide nanoparticles [20] and prepare battery materials [21]. However, there is currently no precedent for using mechanochemical methods to promote the facile doping and reduction of metal oxides.
A recent Perspective from Pacchioni and co-workers suggested a strategy to increase the reducibility of MoO3 by increasing their interfacial areas [22]. In this regard, mechanochemical methods are perfectly suited for increasing the reducibility of MoO3 and, therefore, promoting their facile reduction. However, this route has not been explored so far. In this context and based on our interest in lithium chemistry [23]-[25], we hypothesized that by introducing lithium metal as a reductant and a Li-ion source, and using mechanochemical methods to increase the reducibility of Co3O4, it is possible to deliver facile CoO4 reduction and Li+ doping in a one-pot manner. The findings are reported herein.

Lithium metal (ingots) and Co3O4 (powder) at three different stoichiometric ratios (Li:Co3O4 = 1:1, 2:1 or 3:1) (Scheme 1) were treated in a mechanochemical ball mill using an air-tight Teflon™ jar and a Teflon™-coated steel ball (see Supporting Information for details). We chose Teflon™ as the jar/ball material to avoid the formation of Li-Fe alloys during ball milling. The ball milling frequency and time are key factors that influence the reaction outcomes. We employed a mild 20 Hz frequency to avoid potential thermal runaway. The reactions were conducted in an intermittent manner by stopping the ball milling every 1 to 2 min to check the external temperature of the reaction jar. In all three reactions, we observed a 3 to 5 min induction period (jar temperature did not rise), followed by a 1 to 2 min exothermic reaction period (jar temperature increased to ~35-45 °C). The ball milling processes continued after the exothermic period until the total reaction times reached 15 min to ensure that the reactions were completed.

\[
\begin{align*}
\text{n Li (ingots) + Co}_3\text{O}_4 (\text{powder}) & \xrightarrow[20 \text{ Hz}]{15 \text{ min}} \text{Co metal} \\
& \quad \text{Li}_x\text{Co}_{3-x}\text{O} \\
& \quad \text{LiH} \\
& \quad \text{LiO} \\
\end{align*}
\]

**Scheme 1.** Mechanochemical reactions between Li metal and Co3O4.

A 1:1 Li:Co3O4 reaction leads to the full consumption of Li metal ingots, producing a mixture of a black powder and hard metallic grains (average dimension of the metallic grains is ~2mm). Surprisingly, we found that the metallic grains were ferromagnetic and suspected to be Co metal, as confirmed by EDX SEM (vide infra). In terms of mass balance, 85 wt.% of the input materials were recovered (the rest of the materials stuck to the ball/jar surfaces and could not be retrieved), among which 20–25 wt.% was the Co metal grains and 75–80 wt.% was the black powder.

The black powder was analyzed by powder X-ray diffraction (PXRD) on a silicon zero-background sample holder. The PXRD result suggests that the main phase of the black powder was unreacted Co3O4 with a small amount of Li10Co0.81O [26]-[28] and a second form of Co3O4 (CoO-Co3O4) (Figure 1a). Li10Co0.81O belongs to the family of Li-doped Co(III)O materials, formulated as Li1xCo1–xO (0 < x < 0.2) [26]-[28], which features a rock salt structure and have been widely investigated as precursors to the mainstream commercial Li-ion battery cathode material LCO [29]. From a structural perspective, Li2Co1.81O is a solid solution of Li+ in Co(II)O, with a mixed-valent Co(II,III) structure of general formula Li1.81Co(II,III)xO [29]. To form the solid solution, the traditional method is to heat a mixture of Li2O2 (Li2 source) and CoO at 900 °C [26]-[28]. In comparison, this work demonstrates that Li2Co1.81O materials can be produced under mild mechanochemical conditions (room temperature for 15 min). It is also noteworthy that the powdery products from the 1:1 reaction are not sensitive to air, with their PXRD patterns identical under argon or air.

**Figure 1.** Powder X-ray diffraction data of the powdery products from the 1:1 (a, red), 2:1 (b, blue) and 3:1 (c, green) reactions, along with Li10Co0.81O (ICDD 01-075-0534) (top) and Co3O4 (01-080-1535) (bottom) for comparison.

Since Co3O4 was in excess in the 1:1 reaction, we increased the Li:Co3O4 ratio to 2:1. Similar to the 1:1 reaction, we recovered ~85 wt.% of the materials, among which 35–40 wt.% was Co metal ingots and 60–65 wt.% was a black powder. The PXRD data of the powdery products from the 2:1 reaction indicates that the main phase was Li10Co0.81O, with a small quality of unreacted Co3O4 (less than for the 1:1 reaction) and Li2O (Figure 1b). It is noteworthy that the Co metal ingots increase in both weight percentage and grain size (6–8 mm) compared to the 1:1 reaction (Figure 2a).

The Co metal ingots were covered with a hard shell of black powder. Removal of the shell exposed metallic surfaces, which are stable in air for several days. EDX SEM data of multiple sites on the metallic surfaces (Figure 2b) confirmed an average >85 wt.% of cobalt. Small weight percentages of carbon (7–10 wt.%) and oxygen (2–3 wt.%) are consistently present, probably from the milling jar’s Teflon™ material (for carbon) and the Co3O4 starting material (for oxygen).
Increasing the Li:CoO₄ ratio to 3:1 led to a mixture of Co metal ingots (15–20 wt%) and a dark blue powder (80–85 wt%). The dark blue powder was air sensitive, in contrast to the air-stable black powdery products from the 1:1 and 2:1 reactions. The PXRD data (collected under argon atmosphere) of the dark blue products indicates that it was a mixture of Co(II)O (main), LiₓCo₁₋ₓO (minor), Co (minor), Li (minor), LiH (minor) and Li₂O (minor) (Figure 1c). There is no unreacted CoO₄, but instead, with the presence of unreacted Li.

An overview of the results from the 1:1, 2:1 and 3:1 reactions unveil two trends (Figure 3): (1) Co(II)O is only produced in the 3:1 reaction; (2) Co metal and LiₓCo₁₋ₓO increase from the 1:1 to the 2:1 reaction. The trends suggest that: (1) Co metal and LiₓCo₁₋ₓO may come from the same reaction(s), as their amounts increase simultaneously; (2) Co(II)O may be produced in different reaction(s) from which produced Co metal and LiₓCo₁₋ₓO.

Figure 3. Approximate product concentrations (wt.%) for the 1:1, 2:1 and 3:1 LiₓCoO₄ reactions.

In the literature, LiₓCo₁₋ₓO has been synthesized by oxidation reactions between Li₂O and Co(II)O at 900°C [26] [29]. In comparison, in our mechanochemical reactions, LiₓCo₁₋ₓO was formed by the reduction of CoO₄. Based on our observations, we hypothesize two competing reaction pathways (Figure 4): (1) Li(0) reduces part of the CoO₄ to Co(0), meanwhile Li⁺ dopes into the remaining cobalt oxide, to form the LiₓCo₁₋ₓO; (2) Li(0) reduces the Co(II,III)O₄ to Co(II)O and forms Li₂O. Pathway (1) dominates in the 1:1 and 2:1 reactions, while pathway (2) is favorable in the 3:1 reaction (Figure 4).

Density functional theory (DFT) calculations were used to verify this hypothesis and to further understand the reaction mechanisms between lithium metal and CoO₄. We began by calculating the total energies of the various reactants and products involved in the reactions between Li metal and CoO₄, including the low energy structures for LiₓCo₁₋ₓO (x = 0–0.44), as described in the Computational Details section of the Supporting Information. Based on the reactions proposed in Figure 4 and the reaction products measured in Figure 3, three possible fully balanced reactions are postulated (see Eqs. (S1–S9) in Supporting Information) for each of the three LiₓCoO₄ ratios considered.

Figure 4. Two postulated competing reaction pathways, (1) and (2), and their preferences at different stoichiometric ratios. The stoichiometries of the reaction pathways are not balanced.

As expected, all the calculated reaction energies are strongly exothermic. It is noteworthy that the reactions energies for the three LiₓCoO₄ ratios are reasonably similar, with values ranging from -1.30 to -1.63 eV per Li. Nevertheless, the most favorable reaction energy was found for the 2Li:CoO₄ ratio, in qualitative agreement with Figure 3. Furthermore, these results suggest that there is limited benefit in using high Li metal concentrations (i.e., 3Li:CoO₄) in these reactions as the energetic benefit per Li is negligible or is instead an energetic penalty. These findings support our postulated reaction mechanisms in Figure 4, where Li-doped CoO can be synthesized by the Li-facilitated reduction of CoO₄ to Co and Li doping into the remaining cobalt.
oxide, or via the Li-facilitated reduction of CoO\(_2\) to CoO and the formation of Li\(_2\)O.

With regards to the Li\(^+\) doping concentration, each of the three reaction mechanisms displays a unique trend (Figure 5). For Li:Co\(_{0.4}\), the reaction energy increases with increasing Li, which suggests that, at least thermodynamically, higher Li concentrations in Li\(_{x}\)Co\(_{1-x}\)O should be attainable. In contrast, the opposite trend is observed for 2Li:Co\(_{0.4}\), while in the case of 3Li:Co\(_{0.4}\), the reaction energy is unaffected by the Li dopant concentration considered. These results suggest that the reaction mechanism for Li metal and CoO\(_2\) is likely to change based on the concentration of Li in Li\(_{x}\)Co\(_{1-x}\)O. A complete understanding of these mechanisms requires a range of factors, including reaction conditions and the interfaces of and between Li metal and Co\(_{0.4}\) to be accounted. Such simulations are currently being developed in our research groups and are expected to reveal crucial insights into the mechanochemistry of alkali metal and metal oxides.

For comparison, we also considered the energetics of the conventional solid-state reaction between Li\(_2\)O and CoO used to synthesize Li\(_{x}\)Co\(_{1-x}\)O [26–28]. As shown in Figure S6, the energies for this reaction, from -0.94 to -1.18 eV, are consistently less favorable than the reaction energies presented in Figure 5 for Li metal and Co\(_{0.4}\). This further evidences the potential of using Li metal as a starting material for the synthesis of lithium transition metal oxides materials.

To further understand the Li\(^+\) doping process of CoO resulting from the reaction between Li metal and Co\(_{0.4}\) and to identify the character of the resulting reduced species, we carried out a Bader charge analysis [30] of the lowest energy Li\(_{x}\)Co\(_{1-x}\)O configurations from the DFT calculations. Bader analysis has been previously used to investigate the charge states of numerous species in battery materials [31–33].

The results of the Bader charge analysis for Li, Co and O in Li\(_{x}\)Co\(_{1-x}\)O, as well as their percentage changes as a function of x, are presented in Figure S7. The greatest change in Bader charge (11.33%) as a result of increasing Li doping is found for O. In fact, the change in Bader charge for O is more than double the value obtained for Co (5.05%). The Bader charge of Li (~0.89 e) remains relatively constant at all doping concentrations. These findings suggest a significant level of oxygen oxidation (from -1.27 e at x = 0 to -1.14 e at x = 0.44), in addition to the expected Co oxidation (from 1.27 e at x = 0 to 1.33 e at x = 0.44), as a result of Li doping CoO. Similar results have been observed previously using X-ray photoelectron spectroscopy for both the Li doping of CoO [34] and the deintercalation of Li from LiCoO\(_2\) [35].

At x = 0–0.13 in Li\(_{x}\)Co\(_{1-x}\)O, the additional positive charge resulting from Li doping is localised on nearest neighbor O and second nearest neighbor Co sites to the Li dopants. This is illustrated by Figure S8 for Li\(_{0.06}\)Co\(_{0.94}\)O, where the doped Li ion forms three long (~2.41 Å) and three short (~2.03 Å) Li–O bonds with smaller and larger Bader charges, respectively. These longer Li–O bonds in turn result in shorter Co–O bonds (1.91 and 1.99 Å compared to ~2.11 Å in CoO) and a reduced charge for the adjacent Co ion. For x > 0.13, a mixture of Co and O charge states are found as a result of both localized and delocalized excess charge.

Our combined experimental and computational studies suggest that the formation of Li\(_{x}\)Co\(_{1-x}\)O is preferable with a lower Li metal stoichiometric ratio. On this basis, it is sensible to extrapolate that, instead of a one-react LiCoO\(_2\) 3:1 reaction, introducing the three equivalents of Li metal in a sequential manner would improve the production of Li\(_{x}\)Co\(_{1-x}\)O (Figure 4, pathway 1) and suppresses pathway 2.

Indeed, we found that the sequential reaction not only increased the Li\(_{x}\)Co\(_{1-x}\)O wt.% but also produced doped materials with higher Li contents, such as Li\(_{1.47}\)Co\(_{0.53}\)O\(_{2}\), Li\(_{0.62}\)Co\(_{2}\) and LiCoO\(_2\) (Scheme 2), as postulated from the DFT analysis. In comparison, for the one-pot reactions, even with three equivalents of Li metal, the highest Li-content is Li\(_{1.18}\)Co\(_{0.815}\)O. The presence of unreacted Li metal in the 3:1 one-pot reaction proved that the Li\(_{1.18}\)Co\(_{0.815}\)O is probably the highest possible Li-content in the one-pot context. The limit, nonetheless, was broken by the sequential reactions, which achieve Li\(_{0.62}\)CoO\(_{2}\) and LiCoO\(_2\) (Scheme 2). We also noticed that, different from the one-pot reactions, the Co(II)O was not observed during the sequential reactions. The absence of Co(II)O corroborates our hypothesis of the two competing reaction pathways (Figure 4): Co(II)O would only be produced by pathway 2, which would only happen with excess Li metal. By conducting the reaction sequentially, the Li metal was not present in an excess amount at any moment, thereby suppressing pathway 2.

![Scheme 2. Stepwise reactions between Li metal and CoO\(_2\).](image-url)

In conclusion, by utilizing a powerful experimental-computational approach, we have provided proof of concept for the use of Li metal as a highly efficient reductant and Li-ion source in a new low-carbon pathway to reduce inert CoO\(_2\) and produce Co metal and Li\(_{x}\)Co\(_{1-x}\)O mechanochemically. Compared to the state-of-the-art energy-intensive manufacturing of Li\(_{x}\)Co\(_{1-x}\)O and Co metal, this new mechanochemical approach features substantial potential in reducing the carbon footprint of cathode materials synthesis.

ASSOCIATED CONTENT

Supporting Information.
Full experimental and computational details are included in the Supporting Information.

AUTHOR INFORMATION

Corresponding Authors
Erli Lu – Chemistry - School of Natural and Environmental Sciences, Newcastle University, Newcastle upon Tyne, UK. https://orcid.org/0000-0002-0619-5967. Email: Erli.Lu@newcastle.ac.uk

James A. Dawson – Chemistry - School of Natural and Environmental Sciences and Centre for Energy, Newcastle University, Newcastle upon Tyne, UK. Email: James.Dawson@newcastle.ac.uk

Jamie A. Gould – Faculty of Sciences, Agriculture and Engineering, Newcastle University, Newcastle upon Tyne, UK. Email: Jamie.Gould@newcastle.ac.uk

Author Contributions

N. D. and E. L. designed and conducted the experiments. I. A. G. conducted the EDX SEM experiments and analyzed the data. J. A. D. designed and conducted the calculations and analyzed the data. J. A. G. conducted the PXRD experiments and analyzed the data. E. L. conceptualized the project, overviewed the research and wrote the manuscript with contributions of all authors.

ACKNOWLEDGMENT

The authors thank the Newcastle University Chemistry Technical Support Team (Dr. Laura McCorkindale, Dr. Amy Roberts and Ms. Alexandra Rotariu) and Mr. Gary Day (Chemistry Mechanical Workshop) for supporting our research. E. L. thanks Prof. Steve Bull and Paul Christensen (School of Engineering, Newcastle University) for insightful discussions. E. L. and J. A. D. thank the Newcastle University Academic Track (NUACT) Fellowship Scheme for financial support. N. D. thanks Newcastle University for a NUaCT PhD studentship. J.A.D. gratefully acknowledges the EPSRC (EP/V013130/1) for funding. Via membership of the UK’s HEC Materials Chemistry Consortium, which is funded by the EPSRC (EP/L000202/1, EP/L000202/1, EP/R029431 and EP/T022213), this work used the ARCHER UK National Supercomputing Service. E. L. thanks the EPSRC North East Centre of Energy Materials (NECEM) and the Royal Society of Chemistry Research Enablement Grants (E20-5153) for financial support to build the mechanochemistry facility.

REFERENCES


Mild conditions!

20 Hz
Room temperature
15-45 minutes

Co metal

Li metal

$\text{Li}_x\text{Co}_y\text{O}_z$

$\text{Co}_3\text{O}_4$