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Perspective

# Energy Storage Materials as Emerging Nano-Contaminants

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# Energy Storage Materials as Emerging Nano-Contaminants

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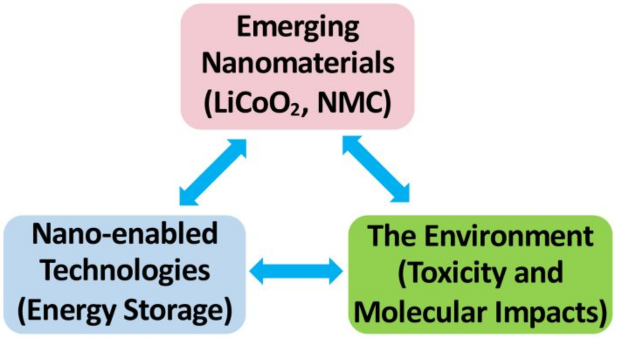
Emerging Nanomaterials ($LiCoO_2$, NMC)
Nano-enabled Technologies (Energy Storage)
The Environment (Toxicity and Molecular Impacts)

**For TOC only**

ABSTRACT. New and emerging nanotechnologies are increasingly using nanomaterials that undergo significant chemical reactions upon exposure to environmental conditions. The rapid advent of lithium ion batteries for energy storage in mobile electronics and electric vehicles is leading to rapid increases in manufacture of complex transition metal oxides that incorporate elements such as Co and Ni that have the potential for significant adverse biological impact. This perspective summarizes some of the important technological drivers behind complex oxide materials and highlights some of the chemical transformations that need to be understood in order to assess the overall environmental impact associated with energy storage technologies.

**Introduction.** The rapid expansion in commercial production of nanomaterials has prompted many studies aimed at understanding the implications of the intentional and unintentional release into the environment and interactions with biological systems.[1-16] These studies have yielded many important insights about the how nanomaterial properties such as size, shape, and surface charge impact their environmental and biological interactions.[1-16]

A common paradigm for risk assessment of nanomaterials is based on three aspects: (1) the mass (or volume) of material produced, (2) potential for release and exposure, and (3) and inherent toxicity of the nanomaterial.[3] Studies to date of nanoparticle impact have focused on nanoparticles currently used commercially in large amounts in consumer applications, such as $TiO_2$, ZnO, Au, and carbon nanotubes.[3, 9] While these have revealed many important aspects of the biological impact of nanomaterial, new nanomaterial composition and structures continue to be developed and commercialized.[9, 17-21] Many of these emerging engineered nanomaterials have complex chemical properties that have not been widely investigated for potential roles in chemical transformations and biological impact, such as oxidation-reduction activity and compositions that include elements with significant potential for environmental or human toxicity.[22-29] A truly proactive paradigm for sustainable development of nano-enabled technologies would need to identify potential adverse environmental and/or toxicological impacts early in the technology development cycle, and if possible take steps to redesign, as needed, the properties of the nanomaterials to yield the greatest overall benefit. Such a proactive paradigm requires taking steps to understand the properties and chemical transformations of emerging classes of nanomaterials in realistic media such as natural waters or biological fluids, and experimentally using validated computational models to predict the chemical properties and biological interactions of nanomaterials in the environment.[30-32] This Perspective highlights the importance of complex transition metal oxides used in energy storage as an emerging class of technologically and environmentally important nanomaterials for future investigation by the nanoscience and environmental science communities.

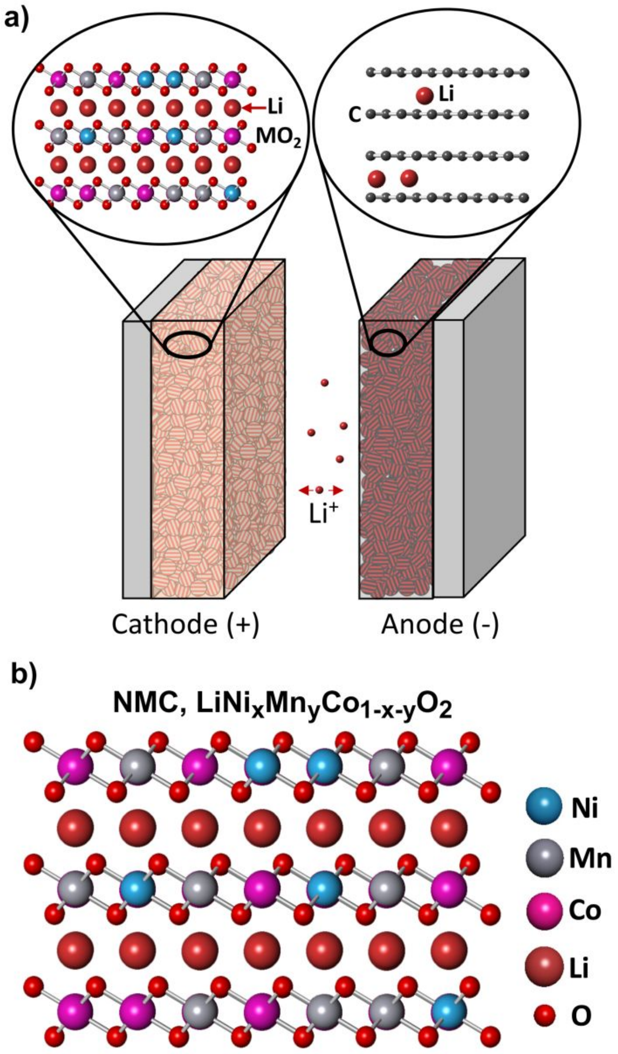

Figure 1: a) Layered structure of lithium intercalation compounds used in lithium ion batteries. Electrodes consist of thin metallic sheets with ~0.1 mm thick layers of deposited nanoparticles and other added electrode components for structural integrity. The active cathode (positive electrode) “NMC” material has an atomic structure with sheets of $MO_2$ (where M=Ni, Mn, or Co) separated by layers of lithium ions. The anode (negative electrode) consists of graphite with lithium intercalated between the layers of graphite. Electrical connections to electrodes are not shown. b) Molecular structure of the NMC class of cathode materials, showing two-dimensional layers of metal oxide ($MO_2$, where M=Ni, Mn, Co) separated by layer of Li ions.

**Energy storage materials.** The explosive growth in the use of lithium ion batteries for mobile electronics (e.g., laptops and cell phones) and electric vehicles has fueled rapid increases in a range of inorganic solid-state materials. Today's commercial lithium ion batteries use cathodes made from lithium intercalation compounds. Batteries used for mobile electronics (cell phones and laptops) and for electric vehicles typically use batteries whose cathodes are comprised of lithium intercalation compounds made from the delafossite crystal structure, consisting of metal (M) ions in the form of $MO_2$ sheets separated by layers of Li ions. $LiCoO_2$ ("LCO") is most common cathode (positive electrode) material used in lithium ion batteries for applications such as cell phones and laptops.[33-34] In recent years the explosive growth in electric vehicle technology combined with the high cost and limited global supply of Co have fueled great interest in replacing Co with Ni, Mn, and other more earth-abundant elements, leading to an entire family of chemical compositions generically known as "NMC" ($LiNi_xMn_yCo_{1-x-y}O_2$) and "NCA" ($LiNi_xCo_yAl_{1-x-y}O_2$), in which the amounts of the transition metals can be varied in a nearly continuous manner.[35-36]

An important motivation for study of energy storage nanomaterials is their large and rapidly escalating volume of manufacture. Many nanomaterials used in emerging technologies, such as nanoparticles as catalysts and nanoparticle-based photovoltaic devices, can be used in very thin films with relatively little bulk material because the underlying chemical and physical processes occur only near the nanoparticle surfaces. In contrast, energy storage compacity scales with the volume (or mass) of the material present. To store more energy, a larger mass of LCO or NMC must be used. Values for volume of LCO/NMC materials being manufactured are not frequently presented directly in the literature, but they can be estimated from a knowledge of the total energy storage capacity of the batteries manufactured. Industry estimates have been reported of 45 gigawatt-hours (GWh) in 2015, 125 GWh in 2020, and projected to be ~220 GWh in 2025.[37] These storage capacities can be translated into LCO/NMC/NCA materials production based on straightforward analysis of materials parameters; the amount of charge stored per unit mass is represented as the specific capacity, in units of milliampere hours per gram (mAh/g). A typical LCO/NMC material can store 150 mAh/g of energy at a voltage of 3.8 V,[38] which then corresponds to energy storage of 0.57 Watt-hour per gram of cathode material. A typical electric vehicle contains approximately 40-50 kg of LCO/NMC/NCA in its battery pack. The 45 GWh production capacity in 2015 then corresponds to 79,000 metric tons of cathode materials, with estimated annual future production of ~200,000 tons in 2020 and 380,000 tons in 2025. Importantly, these production rates are comparable to or larger than the estimated amounts of manufacture of many other nanomaterials such as Ag, $SiO_2$ and $TiO_2$ that have been widely investigated by the nano-EHS community.[39]

**Energy Storage: Why nano?** The biological impact of energy storage materials can be dependent both on their total mass and whether that mass is distributed into large particles or is in a nanostructured form. Smaller particles lead to faster charge and discharge rates and greater mechanical stability, but the advantages of small particle size must be balanced by deleterious effects of uncontrolled surface reactions that shorten battery lifetime.[40] The intercalation and de-intercalation of Li each time a LIB is charged/discharged leads to expansion and compression (shrinkage). $LiCoO_2$ expands and shrinks by approximately 10%. These repeated volumetric changes cause mechanical stresses that can eventually result in fracturing of the larger particles during use and can even create large numbers of nanoparticles *in situ*.[41-43] As one example, Fig. 2 shows scanning electron microscopy (SEM) images of a commercial micron-sized cathode material that was used in a battery and charged and discharged (lithiating and de-lithiating) 200 times. The SEM image shows that the starting micron-sized primary particles have undergone significant fracturing, leading to the formation of many smaller nano-sheets; the sheet-like morphology is a direct consequence of the 2-dimensional nature of the crystal structure (see Fig. 1), which weak bonding between layers of $Li^+$ and layers of $MO_2^-$ (where M=Ni, Mn, Co). These deleterious effects of mechanical pulverization are one of the major driving forces behind used of nanoparticles or 1-dimensional nanowires, as smaller-sized particles are less prone to further fragmentation. Smaller nanoparticles also have lower resistance and allow faster Li intercalation, improving the ability to charge and discharge quickly. However, small nanoparticles are also more difficult to make electrical contact to and may also increase the rate of other adverse chemical reactions that can occur on the electrode surfaces. As a result of these competing factors, the primary particle size of cathode materials used in current-generation electric vehicles is typically on the order of 50-250 nm in size. While this perspective focuses on metal oxides, transition metal phosphates such as $LiFePO_4$ are also used as cathode materials in power tools and stationary energy storage. Because LFP is highly resistive, it is frequently used as ~50 nm particles in a technology sometimes referred to as “super-phosphate” technology. [44-46] On the anode side of the battery, graphite remains the most commonly used material but advanced battery technologies are now including Si in various nanoparticle compositions (e.g., Si, $SiO_2$, silicon oxycarbides) in order to increase their storage capacity.[18, 47] In all cases, smaller particles can yield faster charge/discharge capability that is beneficial for consumer applications.

**Containment and Routes of Exposure.** A second set of factors associated with environmental risk is those associated with release and exposure. It is currently estimated that <5% of lithium ion batteries are recycled, with the rest going into landfills or other non-sustainable disposals.[48] Early generations of lithium ion batteries were often packaged in cylindrical cells with a metal housing that provided strong mechanical protection. More recent designs are frequently based on “pouch cells” in which layers of flat electrodes and other battery components are enclosed in a heat-sealed plastic pouch that can be more easily punctured during or after disposal. The potential for improper disposal and resulting environmental release of lithium-ion battery materials is exacerbated by the fact that efforts to reduce the costs of materials (e.g., replacing Co with less-expensive elements such as Ni and Mn) and manufacturing costs also reduce economic incentives to recycling.[49] Evaluation of metal leaching from commercial cells with $LiCoO_2$ cathodes reported high levels of solubilized Co that significantly exceeded California regulations for classification as hazardous waste. Several states, including New York and California, currently ban the disposal of lithium ion batteries in household trash or landfills due to the toxicity of the associated metals, along with the potential risk of fire.

**Chemical Transformations and Biological Impact.** The third aspect of risk assessment is the inherent biological response and toxicity to the nanomaterials themselves. These materials are also based on compositions that include elements known to be toxic to many organisms, including Co, Ni, and Mn.[50] Based on the above criteria, it is clear that many of the materials used in energy storage present potential routes of exposure due to the large volumes of manufacture and the lack of recycling, with many of the materials present in nanoscale form. Understanding the potential biological impact of complex metal oxides brings with it new chemical mechanisms of toxicity that must be understood. Of importance with complex metal oxides is that in many cases the technological impact is directly connected to the presence of more than one accessible oxidation state. For example, charging a lithium-ion battery the cathode (positive electrode) corresponds to

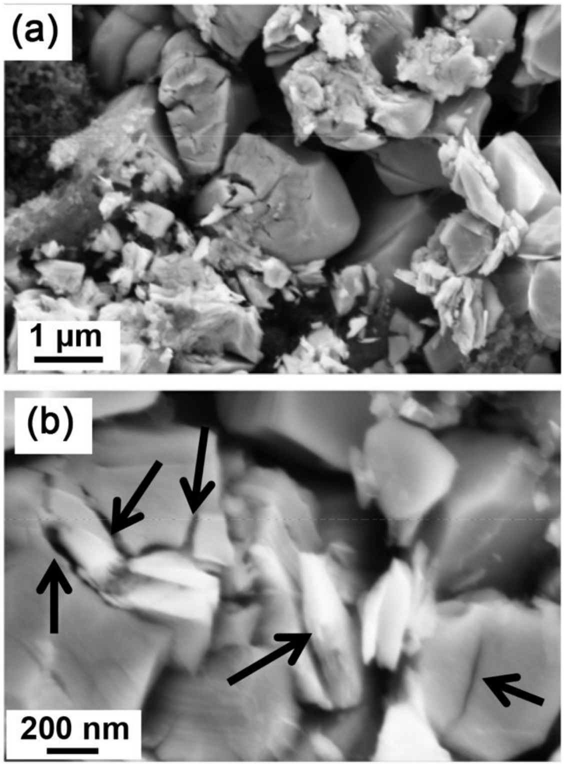

Fig. 2. Scanning Electron Microscope images of NMC-based battery cathode after cycling 200 times, showing fragmentation and formation of 2-dimensional sheet-like nanostructures. a) SEM image showing many individual NMC particles; b) higher magnification image highlighting cycling-induced fracturing of NMC particles at locations indicated by the arrows. Adapted from Hang, et al., Chem. *Mater*. 2016, *28*, 1092−1100.

the reaction $LiCoO_2 + C_6 \rightarrow CoO_2 + LiC_6$, during which the oxidation state of Co is increased from 3+ (in $LiCoO_2$) to 4+ (in $CoO_2$). The operating voltage of the battery and amount of energy stored are inherently controlled by the oxidation potential of the metal ion in the cathode. Co and Ni are widely used because their oxidation potentials, when incorporated into solid-state electrode materials such as $LiNi_xMn_yCo_{1-x-y}O_2$, provide battery operating voltages that yield high levels of energy storage. The presence of multiple oxidation states for Co and Ni materials also makes them useful for other emerging technological applications. For example, Co-based and Ni-based materials have been shown to be highly active catalysts for electrochemical water oxidation, an important element of solar fuel generation.[51-54]An important unifying aspect of these studies is that the technological utility is directly connected to the oxidation-reduction chemistry of the transition metal compounds. In the case of battery materials, energy is essentially stored in the oxidation state of the transition metal. In the case of catalytic materials, their ability to catalyze reactions such as oxidation and reduction of water is due to the fact that Co and Ni have redox potentials that allow them to serve as intermediate electron reservoirs at critical transition states in catalytic reaction.

The above discussion highlights that redox-active transition metal compounds are a particularly important and emerging class of nanomaterials whose impacts on the environment and potential impact on human health remain largely unknown. Unlike many of the nanomaterials studied to date, complex metal oxides have the potential to interact in ways that depend not only on their physical properties (e.g., size, shape, charge) but also by the intrinsic chemical properties of the nanomaterial bulk and the nanomaterial surface reactions. To highlight some of the new chemistry that can be associated with complex metal oxides, we briefly summarize some of the more important observations and lessons learned thus far investigating the fundamental chemical transformations and biological impact of $LiCoO_2$ and related compounds of the NMC family.

An important aspect this work has been the ability to synthesize nanomaterials with different sizes, shapes, and chemical composition. When linked with biological impact studies, these abilities enable a closed-loop in which it is possible to establish structure-function relationships among the class of nanomaterials. These capabilities have been significantly augmented by linking the experimental work with theoretical studies of how the detailed atomic structure of the nanomaterials controls the thermodynamics of transition metal release. We propose that such an approach could be adopted more broadly by the chemistry, materials, and toxicology communities in order to develop testable hypotheses and science-based design rules for how to synthesize compositions and structures with reduced toxicity and other adverse environmental impact.

**A case study of NMC-family nanomaterials**. Initial studies with the Center for Sustainable Nanotechnology using an equistoichiometric composition of NMC ($LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$). Our initial studies showed that the interaction of NMC with cells of *Shewanella oneidensis* MR-1 (a widely known soil bacterium) induce dose-dependent decreases in cell respiration.[55] The initial studies showed that there was little evidence for direct association of the nanoparticles with the cells; furthermore, the impact on Shewanella could be largely (but not completely) reproduced using aqueous mixtures of $Co^{2+}$ and $Ni^{2+}$. Together, these observations indicated the primary mechanism of induced toxicity was due to the chemical transformation of the nanoparticles, releasing free ions that then interacted with the bacteria.[55] However, an unexpected observation was that the different metals were not released at rate expected from the bulk composition of the nanoparticles. In addition to very rapid release of Li, we also observed that Ni was released fastest, followed by Co and then by Mn. Furthermore, the nanoparticle dissolution largely ceased when the nanoparticles achieved a new, altered Mn-enriched composition. These studies highlighted a need to develop methods for characterizing, understanding, and predicting the solubilization of transition metals from within complex materials structures and also provided one example of the ability to establish chemistry-based "design rules" for less-toxic nanoparticles.

Another important advance form this work arose from computational studies coupling density functional calculations of lattice stability with empirical measurements of ion solvation energies.[56-58] This "Hess's Law" approach allows for direct comparison of the thermodynamics of ion release into aqueous media from complex materials such as NMC; these computational studies established, for example, that $Ni^{2+}$ has low stability in NMC in part because the NMC crystal structure places the ions in an octahedral coordination, while $Ni^{2+}$ generally prefers a square planar coordination.[57] The initial experimental and computational studies allowed us to hypothesize that NMC nanomaterials that were enriched in Mn would have reduced biological impact towards Shewanella, and were confirmed by experiment as an example of computationally guided "nanoparticle re-design".[59] Guided by the understanding achieved in the computational studies, we synthesized NMC nanomaterials with higher Mn fractions and confirmed that these "re-designed" nanomaterials indeed had reduced biological impact on *Shewanella*.[59] However, the Mn-enriched nanoparticles also increased the impact on *Daphnia magna*, highlighting the challenges of mitigating environmental impacts across the breadth of environmental species.

A common challenge in assessing toxicity of different nanomaterials is to identify the property way to normalize and/or compare data obtained under different conditions and/or with different sizes. Since release of transition metals is a relatively slow process, we hypothesized that the release should be proportional to the surface area of the material, rather than its mass. To test this hypothesis, we synthesized NMC materials in flake-like form (exposing predominantly the (001) crystal plane, in block form (exposing a broader range of crystal planes, but with smaller surface area), and compared with a commercially available NMC consisting of larger sintered particles of lower surface area yet. Experiments probing the dose-dependent viability of bacteria showed that mass-based dosing yielded very different toxicity for the three materials, but that when the results were normalized by the specific surface area, all three materials collapsed onto a single line. This result established that the fundamental chemical processes that control toxicity of the NMC-class of materials are controlled by surface processes, while being relatively insensitive to the precise atomic configurations of the starting crystal faces.

**Nanoparticle-induced molecular mechanisms.** While our initial studies using bacterial cells indicated that the primary mechanism of toxicity was associated with chemical transformation of the nanoparticles and subsequent release of ions into the aqueous phase, more recent studies using bacteria, eukaryotic cells, higher-level organisms have all shown strong evidence for nanoparticle-specific effects when using lab-synthesized NMC nanoparticles that are typically ~ 80 nm across, and ~ 10 nm thick. Initial studies using *Daphnia magna* as a model system for understanding the effects of nanoparticle release into freshwater aquatic systems showed the exposure of Daphnia to NMC nanoparticles induced clear signs of nanoparticle-specific toxicity, including strong adhesion of NMC nanoparticles to the carapace and impacts on survival and gene expression that greatly exceeded the effects of free-ion controls.[60] These results all point to the nanoparticle-specific impacts in higher-level organisms of relevance to environmental studies.

A key challenge in understanding environmental impact of nanoparticles is the wide diversity of organisms in the environment. Thus, one important challenge is to understand whether there are unifying mechanisms of biological impact that span across different organism, by understanding the molecular-level changes that NMC and related reactive nanoparticles induced in biological systems. For example, studies using the Gram-positive bacterium *B. subtilis* and Gram-negative *S. oneidensis* both showed clear evidence of DNA damage induced by exposure to NMC.[61] DNA damage in *B. subtilis* also was accompanied by changes in expression of genes characteristic of metal uptake, sporulation, oxidative stress, and DNA repair.[61] Similarly, studies showed that the benthic organism *Chironomus riparius (midge)* exhibited significant changes in growth and in gene expression patterns.[62] Figure 3 shows an example demonstrating how $LiCoO_2$ nanoparticles influence a model benthic organism, *C. riparius.* C. riparius frequently live in sediment as larvae, eventually pupating and emerging from the sediment as adult flies. While under normal conditions *C. riparius* larvae are several cm in length and are red in color, exposure to $LiCoO_2$ yielded smaller larvae (<1 cm in length) and changed the color from red to nearly transparent.[62] The change in color is a striking visual manifestation of the influence of Co on heme synthesis. Exposure to $LiCoO_2$ also delayed their emergence as adults. Gene expression studies further confirmed that $LiCoO_2$ induced disruption of genes key to heme synthesis. Importantly, these effects could be partially counteracted by altering the chemical composition to partially substitute Mn for Co in the "NMC" class of materials.[62] The identification of nanomaterial-induced alteration of biochemical processes such as heme synthesis that span across many classes of organisms suggest that there may be key unifying mechanisms of biological impact that span the breadth of organisms in the environment, while the ability to manipulate biological outcomes through intention alteration of nanomaterial composition suggests that it may be possible to generate general chemical principles controlling biological impact of reactive nanomaterials. Ultimately, understanding the fundamental chemical pathways by which NMC, LCO and related nanomaterials impact critical biochemical pathways of toxicity may provide new chemical insights into how to design and synthesize new nanomaterial compositions and structures with reduced biological impact.

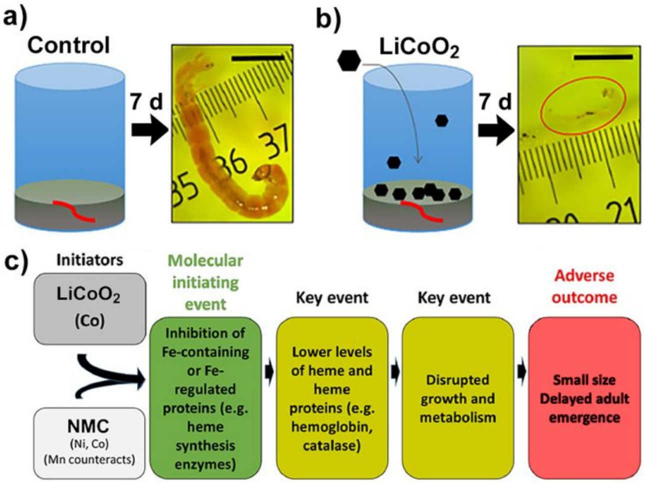

Figure 3: Inhibition of heme synthesis and growth of *Chironomus riparius* due to exposure to $LiCoO_2$ and NMC. a) Optical image of control sample showing emergence of red-colored larvae several cm in length; b) Optical image of $LiCoO_2$-exposed sample, showing inhibited growth and nearly transparent color. c) Graphic depicting how Co (from $LiCoO_2$) and both Co and Ni (from $LiNi_xMn_yCo_{1-x-y}O_2$ "NMC") initiated molecular changes in proteins that lead to reduced levels of heme and hemi-related proteins, disrupting growth and metabolism. Ultimately, these molecular changes become manifest as delayed emergence and small size of the larvae. Scale bars if images are 1 cm in length. Adapted with modifications from from *Environ. Sci. Technol.* **2019**, *53*, 3860-3870.

Recent work using *Shewanella oneidensis* MR-1 demonstrated the development of permanent resistance upon chronic exposure to NMC, allowing the bacteria to survive at much higher concentrations.[63] The adaptation persists even after the Shewanella has been grown for multiple generations, demonstrating that it is a true permanent resistance. The presence of metal-resistant bacterial could be useful, for example, in development of bioreactors to aid in the recovery and recycling of NMC and related nanomaterials.

**Frontier and future studies**. The above results clearly demonstrate that the NMC-class of emerging nanomaterials induces toxicity in a wide range of organisms. A key question looking ahead is to identify what are the fundamental chemical processes that control the biological impact. One intriguing question is to understand what role the high valence state and associated oxidation-reduction reactions induced by the transition metals plays. While the importance of biologically induced reactive oxygen species (ROS) is well established, high-valence transition metal oxides also have the ability, under some conditions, to directly produced reactive oxygen species (ROS).[64] The potential importance of these pathways to biological toxicity remains largely unexplored, but the possibility of forming ROS species that can then initiate further chemistry represents a potentially important pathway to biological response. For example, one overall pathway could be the reaction:

$2H^+ + LiCoO_2 \rightarrow Co^{2+} + Li^+ + 2OH^- + 1/2H_2O_2$, directly producing hydrogen peroxide. The overall standard free energy of this reaction can be estimated using known thermodynamic parameters[65-66] to be -49 kJ/mole of $LiCoO_2$.. The negative value of overall $\Delta G^0$reaction clearly establishes that the interaction of $LiCoO_2$ with water has the ability to directly produce $H_2O_2$ in the course of releasing $Co^{2+}$ ions. The ability of free cobalt ions to generate hydroxyl radicals via Fenton-like chemistry has also been noted previously.[67] In the case of $LiCoO_2$ and related NMC materials, the $Co^{3+}$ is formally in the 3+ oxidation state, which is thermodynamically unstable in water. Consequently, release of Co in the more thermodynamically stable $Co^{2+}$ state must be accompanied by an oxidation process such as formation of $O_{2(gas)}$, •OH (hydroxyl radical), or

$H_2O_2$. From a chemical perspective, understanding the potential role of reactive oxygen species remains an important area of research for studies of nanoparticle-induced biological response. In studies of $LiNiMnCoO_2$ "NMC" compositions, we obtained evidence for formation of ROS species using fluorescent probes that changed with composition, demonstrating highest production of inorganic ROS and highest toxicity from nanoparticles containing the highest concentrations of Ni and Co.[59]

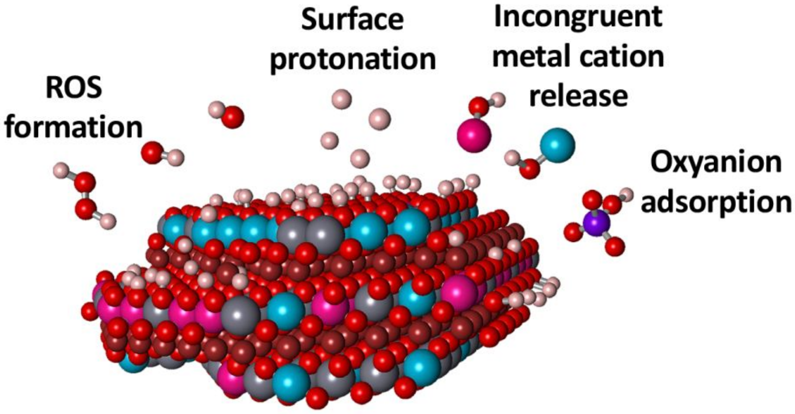

Figure 4: Summary of some of the important chemical processes that control the biological and environmental impact of the NMC-class of complex oxide nanomaterials.

**Summary:** The emergence and commercialization of new nanomaterials will continue to poise potentially new mechanisms of chemical transformation and biological interaction that underlie the potential impacts of nanomaterials to humans and in the environment. Among emerging nanomaterials, those used in high volume and/or incorporating elements with potential toxicity to environmental organisms and/or humans represent a frontier areas for future research. Understanding the fundamental chemical mechanisms of nanoparticle transformations and biological impact has the potential to lead to unifying mechanisms of nanoparticle interactions that cross across different levels of biological organization and link fundamental understanding of nanoparticle chemistry to their resultant biological impacts.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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## ABBREVIATIONS

NMC Nickel Manganese Cobalt; LCO Lithium Cobalt Oxide; NCA Nickel Cobalt Aluminum ; SEM Scanning Electron Microscopy

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