Nanotechnology for Cathode Materials in Lithium-Ion Batteries

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Abstract. In order to provide the energy and power requirements of various uses, people demand for better cathode materials for lithium-ion batteries. Common examples of these include portable electronic gadgets, electric cars, and industrial-sized energy banks. However, most cathode materials have inherent limitations that limit their rated capacity. This limitation is caused by sluggish ion diffusion inside the crystal structure, and the issue is exacerbated for certain materials by their low bulk electrical conductivity. It has been proven that nanostructuring and analyzing cathode materials is, not only a beneficial approach to overcoming this problem, but also extremely useful in making certain materials electrochemically active. Not only does this improve how quickly batteries can accomplish their tasks, but it also makes certain materials more electrochemically active. In this article, recent developments in the design and synthesis of nanomaterials will be introduced. First, the fabrication method, crystal structure, and optimum shape of $LiFePO_4$ nanomaterials were shown. Next, the capacity fading of $LiMn_2O_4$, the crystal structure of $LiCoO_2$, the stable cycle under high pressure, and the difficulties encountered were covered. The study of three distinct nano-cathode materials has shown the important role that nanomaterials play to enhance the functionality of cathodes in lithium-ion batteries.

Keywords: Cathode materials, Li^+ batteries, nanomaterial, development.

1. Introduction

The world's demand for energy is rising to keep up with the needs of contemporary society. Power is derived from various sources, and while they vary by nation, it primarily depends on nonrenewable resources and that will lead to several issues, the most significant of which is the emission of greenhouse gases (GHGs), primarily carbon dioxide, which not only contributes to health problems caused by exposure to polluted air, but also to the harmful effects of global warming, also known as the increase in Earth's surface temperature. Fossil fuels are also limited and non-renewable energy sources [1]. Since the groundbreaking work of Galvani and Volta, batteries have been understood for more than 200 years. They only became highly significant with the invention of the telegraph, the radio, and automobiles. (Figure 1) It has been shown a schematic depiction of a typical lithium-ion battery, including all of its constituent pieces and the path taken by the lithium ions inside the battery. Most commercial batteries use graphitic carbon as the negative electrode, with a maximum potential energy density of 372 $mAhg^{-1}$ and an actual energy density of 330 $mAhg^{-1}$. A layered oxide, such as $LiFePO_4$ with academic and existing capabilities of 274 and 140 $mAhg^{-1}$, serves as the positive electrode's "cathode." Lithium salt ($LiPF_6$), carbonate solvents (both aprotic and nonaqueous), serves as the electrolyte.

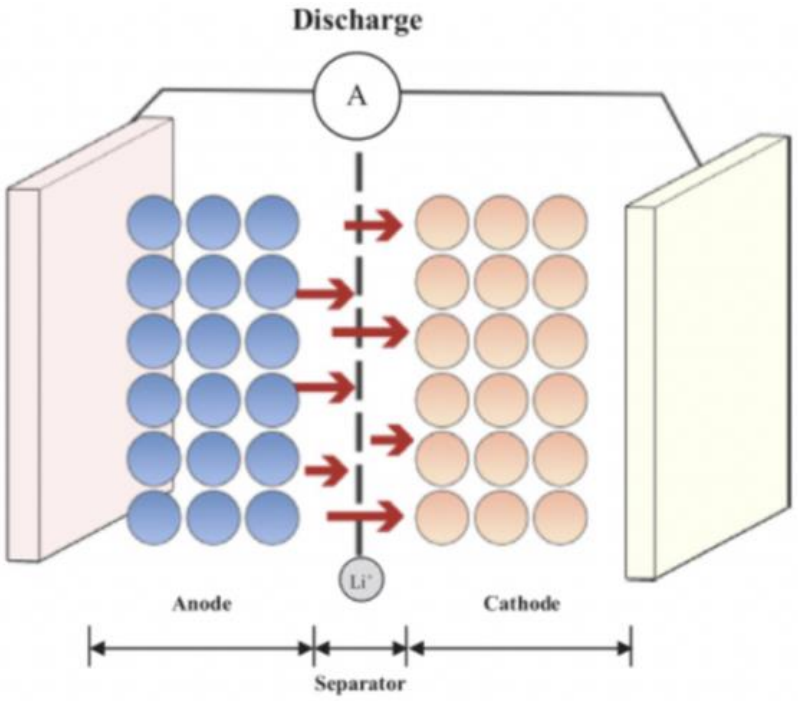

Figure 1. Lithium-ion battery design using regular electrodes [2]

All regions of the world, including different industries (academics, business, government, and the general public), have started to investigate and comprehend the advantages and benefits of nanotechnology over the past 20 years. The two critical facets of nanotechnology are the creation of novel materials and technological advancements with smaller "nano" dimensions. Nanotechnology has advanced quickly during the last 20 years, and numerous nanomaterials (Figure 2) have been created [3].

Although the advantages of nanotechnology and nanomaterials, in general, have not yet to be realized entirely, some goods, including those used in cosmetics, have already entered the market. As a result, the market is flooded with several conventional battery options. Although the full potential of these batteries has not been realised as of yet, they can be improved with some aid from nanotechnology [4]. For instance, nanosized materials may reduce the Li^+ diffusion route and provide a larger surface area for Li^+ exchange due to their high surface-to-volume ratios made possible by nanotechnology. Among the many types of batteries on the market, lithium-ion batteries (LIBs) have quickly become the industry leader because they are the most promising and are evolving at the quickest pace.

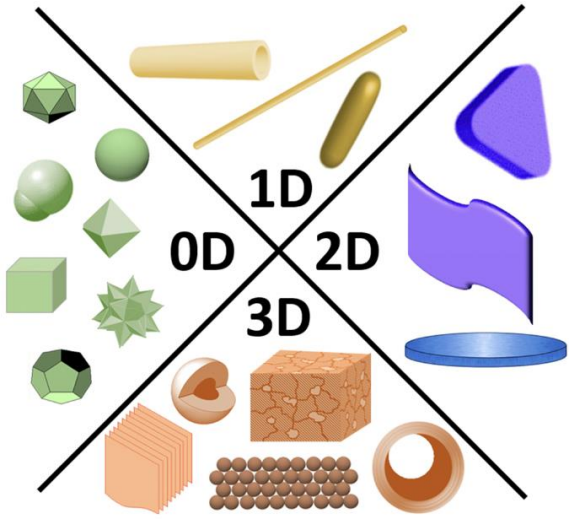

Figure 2. Different shapes of nanomaterials [5]

Within recent memory, batteries have made remarkable advancements. They are widely employed and accepted by the market in various applications, including those for portable electronics, electric vehicles, and airplanes. This paper focuses on nanotechnology and LIBs, with nanotechnology receiving the most excellent attention. However, the potential and scope of nanotechnology can extend to several other battery technologies rather than being restricted to simply LIBs. Even though batteries, particularly LIBs, are ubiquitous in today's world of portable gadgets that battery technology has reached its pinnacle of development. However, Lithium-ion battery cathode material still has a number of technological limits on battery performance in areas such as Energy density, energy supply speed and service life. As a result, an important part of improving battery cathode materials is the use of nanotechnology in their design, synthesis, and engineering modification.

2. Application of Nanotechnology in Different Cathode Materials

2.1. $LiFePO_4$ Nano-Materials for Cathode

Since Goodenough's group made their discovery, phospho-olivine $LiFePO_4$ (LFP), lithium rechargeable batteries might use this as a positive electrode material [6]. LFP is of great interest because at low to intermediate current densities, this cathode material has the maximum capacitance, and it is cheap and non-toxic. However, LFP has a very poor bulk electronic conductivity, which could lead to capacity losses during high-rate discharge. Therefore, it is common to practice employing carbon additives or an LFP matrix when serving as lithium-ion battery cathodes to boost electronic conductivity.

2.1.1. Preparation of LFP nanoparticles

Several samples of nanoparticles of $LiFePO_4$ are prepared via a solid-state process. Samples of $LiFePO_4$ with A-type nanoparticles are made by combining lithium carbonate [Li_2CO_3], ammonium dihydrogen phosphate [$NH_4H_2PO_4$]. The B-type samples are synthesized using Li_2CO_3 and $FePO_4(H_2O)_2$. The precursors are completely mixed in isopropanol in a stoichiometric quantity. When the mixture has been dried, it is heated in a reducing atmosphere for 8 hours at 700 degrees Celsius. Using $C_{12}H_{22}O_{11}$ and $[C_6H_7O_2(OCOCH_3)_x(OH)_{3-x}]_n$ as carbon precursors in a C_3H_6O solution, carbon-coated C-LiFePO4 is synthesised in the following way. The powder free of carbon and the carbon precursors are combined. In $LiFePO_4$, the dry additive has a carbon content of 5%. The mixture is dried before being heated for 4 hours at 700°C in an argon environment. About one weight percent of the material is represented by the amount of carbon coat (C-detector, LECO Co., CS 444) [7].

2.1.2. The Crystal Chemistry of $LiFePO_4$

The structure of $LiFePO_4$ is characterized by a metal framework made up of MO_6^{n+}octahedra joined to each other by PO_4^{3-} tetrahedra (Figure 3). It is possible to see that the Li^+ ions are housed in the structure in four one-dimensional tunnels that are parallel to the 010 direction and intersect the planes of corner-sharing MO_6^{n+} octahedra. Reversible delithiation of $LiFePO_4$ can result in $FePO_4$. At compositions $Li_{1-\Delta}FePO4$ and $Li_{\theta}FePO_4$, with and being 0.05 and 0.11 for macroscopic grains at room temperature, respectively, both phases coexist. These values rise as the temperature rises and, for nanocrystals, as the grain size shrinks. The miscibility gap is said to vanish for macroscopic grains at about 200°C and to be nonexistent for grain sizes under 25 nm^{-5}, even at room temperature. In addition to its performance, the redox pair LFP and $FePO_4$ is a suitable positive electrode due to its environmental friendliness. Although compared to the very high voltage electrodes, the voltage which demonstrate four to five volt vs. lithium, That's an issue, although it arises seldom, when considering safety under heavy power demands. However, poor transport qualities, particularly Li's low chemical diffusivity, are a significant issue for high-power performances. The enhancement of these properties by homogeneous or heterogeneous doping is one option.Another is to optimize shape by nanostructuring, which requires nanosized powder to allow for electrolyte access and warrants

electronic availability, necessitating the construction of mixed conducting networks. Recently, this was accomplished by combining C/RuO_2 coating with nanostructuring.

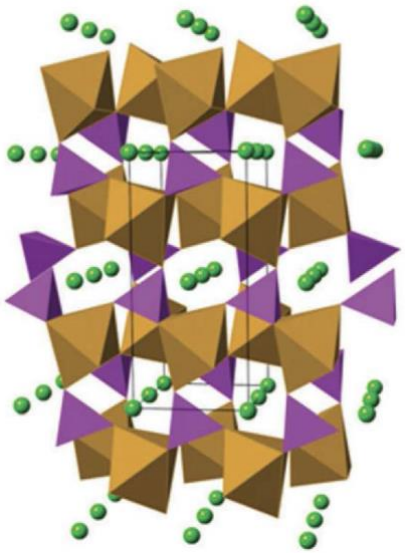

Figure 3. Crystal structure of $LiFePO_4$ olivine [8]

2.1.3. Morphology of Optimized $LiFePO_4$ Particles

SEM and HRTEM have been used to have a look at the $LiFePO_4$ particles' carbon coatings and how they look on the surface. According to the analysis of SEM images, the powders are made up of smaller particles. that are dispersed uniformly and are just slightly clumped together, and exhibit a limited number of pieces. The SEM observation reveals comparable pictures across the sample, which is homogenous at a scale significant in relation to the region under investigation. The average particle size is 2×10^2 nm. The HRTEM may be used to see the many microscopic primary particles that make up each of the secondary particles. Scherrer's law applied to the XRD pattern reveals that their main particles are polydispersed with a mean size of 90 nm. As a result, the main particles are $LiFePO_4$ polycrystallites, which are composed of a few (on average three) monocrystallites. The TEM images provide a clear illustration of the amorphous carbon layer [9]. The interstitial grain-boundary area exhibits a network development of carbon, which may help to explain why $LiFePO_4$ crystals have a continuous electrical potential between them. The carbon covering encircling the main particle appears as the grey zone in the micrographs, while the crystals of LiFePO4 may be seen as the darker areas. Estimated average thickness is 30 nm. Although the SEM and HRTEM pictures of the carbon film show an uneven covering of crystallites due to the carbon film's high porosity, the connection between the particles is what matters for electronic conductivity. The SEM and HRTEM photos clearly show LiFePO4 crystals with a carbon coating, which is a succinct summary of these findings.

2.2. $LiMn_2O_4$ Nano-Materials for Cathode

Although it has a slightly lower total capacity, the spinel structure is more suitable because it can extract all the lithium ions that are present in the material and has superior thermal stability. In contrast, $LiMn_2O_4$ is comparable to $LiFePO_4$, which is more cost-effective and ecologically beneficial. With a starting temperature of over 200°C and a slow heat release rate, $LiMn_2O_4$ has relatively little reactivity when it is charged [10]. Spinel typically has a capacity of around 148 $mAhg^{-1}$, whereas layered oxides rich in nickel total 180–200 $mAhg^{-1}$. The full power of $LiMn_2O_4$ is roughly 120 $mAhg^{-1}$, and the maximum reading is 4 V. Lithium's diffusion coefficient is low, even by comparison to LiCoO2 standards, by a factor of two and ranges between 10^{-10} and 10^{-12} cm2 s.

2.2.1. The Capacity Fade of $LiMn_2O_4$

The disproportionation reaction of trivalent manganese produces divalent manganese and tetravalent manganese, ionic species that are able to migrate across the electrolyte and deposit on the

anode, $LiMn_2O_4$'s capacity fade is relatively high, but this is not the case with LiMn2O4, which contains lithium and nickel. However, at 90-95 $mAhg^{-1}$, the capacity is only somewhat high [11]. However, it appears that because $Li_4Ti_5O_{12}$ operates at a greater operating voltage than graphite, replacing $Li_4Ti_5O_{12}$ with graphite as the anode material reduces capacity fading by avoiding Divalent manganese ion plating at the anode. After 160 C cycles at 50 °C, the material is still in good shape, $LiMn_2O_4$ was used as the cathode material, while $Li_4Ti_5O_{12}$ was used as the material to made cathode, to create lithium-ion cells with a capacity of 90 $mAhg^{-1}$ [12].

2.2.2. Preparation of $LiMn_2O_4$

$LiMn_2O_4$ crystallizes as a spinel has the chemical formula Fd-3m. The Li^+ diffusion is also three-dimensional because of the three-dimensional crystal structure. The performance of batteries can be improved by creating nanostructured materials via synthesis with carefully regulated shape, size, and construction; nevertheless, for $LiMn_2O_4$ to have good stability, good crystallinity is required [13-15]. $LiMn_2O_4$ can be easily made into nanoparticles using the sol-gel and combustion processes. However, the crystallinity is usually not very good., and putting the powders via heat treatment will make them grainier. Nevertheless, as a result of lithiation, b-MnO_2 nanorods are converted into $LiMn_2O_4$ nanorods. can withstand heat treatment at 700 ℃, improving crystallinity without causing particle coalescence. Similar to commercial powder 110 $mAhg^{-1}$ at C/10 is accomplished [16]. Still, When compared to commercial powder, which only has a rate capacity of 50 $mAhg^{-1}$, the nanorods have a substantially higher C rate capability, at 95 $mAhg^{-1}$.

Shaju et al. also used a one-pot resorcinol-formaldehyde method to create a stoichiometric nano-$LiMn_2O_4$. How well the material performs in a battery at both low and high temperatures were enhanced compared to the sol-gel method-prepared material because the nanoparticles are fused and create a porous morphology.

2.3. $LiCoO_2$ Nano-Materials for Cathode

Its extraordinary conductivity and extraordinarily high volumetric energy density make it a great conductor, $LiCoO_2$ (LCO), the most typical cathode in 3C devices, which Sony originally marketed in 1991 [17]. In addition, the most attractive thing is that under the action of high voltage, the released energy of LCO is significantly improved, and the energy density can also be increased by more than 25% [18]. Maintaining a long-term stable cycle of LCO, which can work under high pressure is a major difficulty faced by academia and industry.

2.3.1. The Challenge of $LiCoO_2$ Materials

It can be continuously operated at high voltage with no phase change by doping it with a single element or a combination of elements [19]. Recent studies have emphasized the severity of surface concerns despite the lack of consensus, as the interface is more susceptible to high voltage than the LCO bulk [20]. The deep delithiation state of the cathode is indicated by a high cut-off voltage. After charging, lithium is lacking on the surface region due to the gradient in lithium concentration. Since the atomic orbitals of cobalt elements overlap, oxygen elements in LCO participate in the reaction for charge compensation, and Oxygen and Cobalt with high oxidation states may react with the interfacial electrolyte, resulting in a useless catholyte interface. Evidence suggests that structural failure and voids in the oxygen started at the surface and moved into the inside. The structural integrity of the LCO layered structure is irreparably harmed by Oxygen and Cobalt loss because the CoO_6 plane serves as its framework. There is more exposed area in touch with the electrolyte, which results in better conductivity, there will be more surface structure deterioration and interphase side reactions, which will significantly slow Li-ion diffusion and exacerbate crystal fragmentation, generating a vicious cycle.

2.3.2. The Improvement of $LiCoO_2$ Materials

It is necessary to have a surface coating structure with the following qualities to protect LCO from the surface concerns mentioned above and to ensure at high voltages with steady cycling: a solid

barrier to keep LCO away from the electrolyte, a quick Li^+ conductor to reduce the gradient of the lithium concentration. Traditional surface preparation methods can only be used for physical barriers; Traditional surface coatings made of oxides, phosphates, and fluorides just keep things from getting in or out. $LiMn_{1.5}Ni_{0.5}O_4$ is an electrode material that can overcome this problem and obtain high cycling performance, but it will definitely lead to the dissolution of transition metal ions. Since this solid conformal structure may avoid lattice mismatch, stop interfacial side reactions, and restrict phase transition, it has been used in several works in recent years to safeguard the surface of LCO. One example is this transition layer or solid solution layer. For example, at voltages above 4.55 V, the dangerous irreversible phase shift was stopped by a surface-modified made by Lithium, Aluminium and Fluorine, $LiCoO_2$ with a Lithiu, Aluminium, Cobalt, Oxygen and Fluorinesurface doping layer. Additionally, the reaction of LCO resulted in the production of spinel phases and Li_3PO_4, which enhanced the performance when it is room temperature. However, none of the three objectives were simultaneously met by these solutions. Sadly, They didn't do the full-cell pouch test at high voltages, as needed by the industry (4.5 V).

In order to provide several safeguards, an outside-in oriented nanostructure (OIN-LCO) was built on the surface of a single crystal of outside-in nanostructure LCO, according to how an electrochemical stabiliser works, Li promoter, and something that stops O loss. There are three functional surface layers in the OIN-LCO: 1) $Li_2CoTi_3O_8$ particles are physically isolated from electrolytes, notably HF, by being encased in an LiF coating layer that is very thin (2-3 nm). This stops side reactions at the interface, such as the dissolution of Cobalt ions. Both $Li_2CoTi_3O_8$ and the thin LiF layer that covers it have good lithium-ion diffusion coefficients and are electrochemically stable. 2) Li moves from the inside to the surface, is bridged by a transition phase that looks like spinel and has traces of Ti and F, which also avoids lattice mismatch. 3) The lattice O is stabilised, and the phase change to Li-retarded spinel is permanent, which is prevented by a F-doped layer with a gradational gradient that extends 100 nm below the bulk's covering layer. Calculations using the density functional theory (DFT) show that in a severe delithiation condition, Li diffusion is facilitated by F doping. This demonstrates that incorporating nanotechnology into the production of a nano-thin layer not only protects the LCO cathode material, but also improves the performance of the $LiCoO_2$ cathode material, and so improves the performance of the lithium-ion battery.

3. Conclusion

This article goes into great detail about the advantages of three cathode nanomaterials for their electrochemical and battery capabilities. It has been discovered that cathode materials' structural characteristics in nano-LFP correspond with their electrochemical performance. Only by tightly regulating the synthesis conditions can materials be produced that function well at high current densities. In the case of LMO, the most efficient way to maximise crystallinity without inducing particle agglomeration is to choose an appropriate preparation procedure. The particles' high performance in Li^+ batteries is due to their capacity to intercalate Li ions, which was found to be significantly influenced by distribution of ions throughout the structure in one dimension, shape, and growth direction of the particles. To avoid quick capacity fading in spinel, nanometer-sized particles must be firmly crystalline. For LCO, on LCO crystals, a three-layer, outside-in orientated nanostructure is built, it protects the cathode and electrolyte by lowering the energy required for Li ion migration and stabilising the lattice oxygen due to F doping. Increasing the diffusion in crystalline solid cathode materials has been shown to improve battery performance, and there is a wealth of research demonstrating the advantages of nanostructuring and nanofabrication in overcoming these limitations, hence raising the cycle life and energy density of the battery. Following analysis of the three nanomaterials, it was shown that nanomaterials and nanotechnology significantly enhance the functionality of electrode cathode materials.

References

[1] Gao, Y., Wang, X., Wang, W., Zhuang, Z., Zhang, D. and Fang, Q., 2010. Synthesis, ionic conductivity, and chemical compatibility of garnet-like lithium ionic conductor Li5La3Bi2O12. *Solid State Ionics*, 181 (31-32), pp. 1415 - 1419.

[2] Cook, T. R., Dogutan, D. K., Reece, S. Y., Surendranath, Y., Teets, T. S., & Nocera, D. G. (2010). Solar energy supply and storage for the legacy and nonlegacy worlds. *Chemical reviews*, 110 (11), 6474 - 6502.

[3] Ozin, G. A., & Arsenault, A. (2015). Nanochemistry: *a chemical approach to nanomaterials*. Royal Society of Chemistry.

[4] Abu-Lebdeh, Y., & Davidson, I. (Eds.). (2012). *Nanotechnology for lithium-ion batteries*. Springer Science & Business Media.

[5] AbdelHamid, A. A., Mendoza-Garcia, A., & Ying, J. Y. (2021). Advances in and Prospects of Nanomaterials' Morphological Control for Lithium Rechargeable Batteries. *Nano Energy*, 106860.

[6] Herle, P. S., Ellis, B., Coombs, N., & Nazar, L. F. (2004). Nano-network electronic conduction in iron and nickel olivine phosphates. *Nature materials*, 3 (3), 147 - 152.

[7] MacNeil, D. D., Lu, Z., Chen, Z., & Dahn, J. R. (2002). A comparison of the electrode/electrolyte reaction at elevated temperatures for various Li-ion battery cathodes. *Journal of power sources*, 108 (1-2), 8 - 14.

[8] Chen, S., Jeong, S. R., & Tao, S. (2022). Key materials and future perspective for aqueous rechargeable lithium-ion batteries. *Materials Reports: Energy*, 100096.

[9] Shin Y, Manthiram A (2003) High rate, superior capacity retention LiMn2-2yLiyNiyO4 spinel cathodes for lithium-ion batteries. *Electrochem Solid State Lett* 6 (2): A34 – A36.

[10] Gao, Y., & Dahn, J. R. (1996). Synthesis and Characterization of $Li^{1+}{}_{x}\ Mn^{2-}{}_{x}\ O_{4}$ for Li-Ion Battery Applications. *Journal of the Electrochemical Society*, 143 (1), 100.

[11] Blyr, A., Sigala, C., Amatucci, G., Guyomard, D., Chabre, Y., & Tarascon, J. M. (1998). Self-Discharge of LiMn2 O 4/C Li-Ion Cells in Their Discharged State: Understanding by Means of Three-Electrode Measurements. *Journal of the Electrochemical Society*, 145 (1), 194.

[12] Kanamura, K., Dokko, K., & Kaizawa, T. (2005). Synthesis of Spinel LiMn2 O 4 by a Hydrothermal Process in Supercritical Water with Heat-Treatment. *Journal of the Electrochemical Society*, 152 (2), A391.

[13] Kim, D. K., Muralidharan, P., Lee, H. W., Ruffo, R., Yang, Y., Chan, C. K., ... & Cui, Y. (2008). Spinel LiMn2O4 nanorods as lithium-ion battery cathodes. *Nano letters*, 8 (11), 3948 - 3952.

[14] Wang, L., Chen, B., Ma, J., Cui, G., & Chen, L. (2018). Reviving lithium cobalt oxide-based lithium secondary batteries-toward a higher energy density. *Chemical Society Reviews*, 47 (17), 6505 - 6602.

[15] Zhang, J. N., Li, Q., Ouyang, C., Yu, X., Ge, M., Huang, X., ... & Li, H. (2019). Trace doping of multiple elements enables stable battery cycling of LiCoO2 at 4.6 V. *Nature Energy*, 4 (7), 594 - 603.

[16] Wang, L., Ma, J., Wang, C., Yu, X., Liu, R., Jiang, F., ... & Cui, G. (2019). A Novel Bifunctional Self-Stabilized Strategy Enabling 4.6 V LiCoO2 with Excellent Long-Term Cyclability and High-Rate Capability. *Advanced Science*, 6 (12), 1900355.

[17] Liu, T., Yu, L., Liu, J., Lu, J., Bi, X., Dai, A., ... & Amine, K. (2021). Understanding Co roles towards developing Co-free Ni-rich cathodes for rechargeable batteries. *Nature Energy*, 6 (3), 277 - 286.

[18] Zhou, A., Lu, Y., Wang, Q., Xu, J., Wang, W., Dai, X., & Li, J. (2017). Sputtering TiO2 on LiCoO2 composite electrodes as a simple and effective coating to enhance high-voltage cathode performance. *Journal of Power Sources*, 346, 24 - 30.

[19] Gu, R., Cheng, T., Ma, Z., Qian, R., Lyu, Y., Nie, A., & Guo, B. (2019). Enhanced cycling stability of high voltage LiCoO2 by surface phosphorylation. *Journal of Alloys and Compounds*, 803, 348 - 353.

[20] Wang, C. W., Ren, F. C., Zhou, Y., Yan, P. F., Zhou, X. D., Zhang, S. J., ... & Sun, S. G. (2021). Engineering the interface between LiCoO 2 and Li 10 GeP 2 S 12 solid electrolytes with an ultrathin Li 2 CoTi 3 O 8 interlayer to boost the performance of all-solid-state batteries. *Energy & Environmental Science*, 14 (1), 437 - 450.