

In Situ Chemical Synthesis of Lithium Fluoride/Metal Nanocomposite for High Capacity Prelithiation of Cathodes

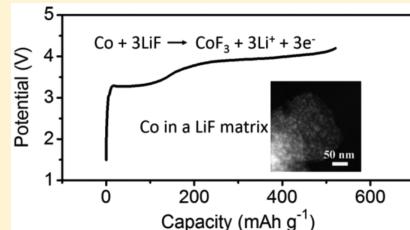
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S Supporting Information

ABSTRACT: The initial lithium loss during the formation stage is a critical issue that significantly reduces the specific capacity and energy density of current rechargeable lithium-ion batteries (LIBs). An effective strategy to solve this problem is using electrode prelithiation additives that can work as a secondary lithium source and compensate the initial lithium loss. Herein we show that nanocomposites of lithium fluoride and metal (e.g., LiF/Co and LiF/Fe) can be efficient cathode prelithiation materials. The thorough mixing of ultrafine lithium fluoride and metal particles (~5 nm) allows lithium to be easily extracted from the nanocomposites via an inverse conversion reaction. The LiF/Co nanocomposite exhibits an open circuit voltage (OCV, 1.5 V) with good compatibility with that of existing cathode materials and delivers a high first-cycle “donor” lithium-ion capacity (516 mA h g⁻¹). When used as an additive to a LiFePO₄ cathode, the LiF/Co nanocomposite provides high lithium compensation efficiency. Importantly, the as-formed LiF/metal nanocomposites possess high stability and good compatibility with the regular solvent, binder, and existing battery processing conditions, in contrast with the anode prelithiation materials that usually suffer from issues of high chemical reactivity and instability. The facile synthesis route, high stability in ambient and battery processing conditions, and high “donor” lithium-ion capacity make the LiF/metal nanocomposites ideal cathode prelithiation materials for LIBs.



KEYWORDS: LiF/metal nanocomposite, cathode prelithiation, conversion reaction, high capacity

Rechargeable lithium-ion batteries (LIBs) have wide-ranging applications as power source for portable electronics, electric vehicles, and grid storages. To meet the ever-increasing energy storage demand of modern society, much effort has been put into developing LIBs with higher energy and power densities.^{1–5} During the first charge process of a LIB (the so-called “formation stage”), the organic electrolyte decomposes and forms a solid electrolyte interphase (SEI) on the anode surface.^{6–8} This process consumes lithium from the cathodes (e.g., LiCoO₂ and LiFePO₄) and thus reduces the specific energy and energy density of LIBs (typically 5–20% of a total battery capacity). To address this problem, electrochemical prelithiation was explored.⁹ However, the complex operation processes and instability in ambient atmosphere make it not suitable for scale-up. Recently, some prelithiation materials to electrodes have been developed as a secondary lithium source to compensate the initial lithium loss during the SEI formation process, and hence an increased overall capacity and energy density can be expected.^{10–13}

In general, the prelithiation materials should have high specific and volumetric capacities as lithium-ion donors. Stability is another important factor for a good prelithiation material. There are several levels for stability, which have different requirements for the battery fabrication processes: (1) Compatibility with the existing electrolyte and no/minimum

undesirable side reaction during the lithium-ion donation process, which is the basic requirement for prelithiation reagents. (2) Chemical stability or slow reaction kinetics with air, so that we can process the electrode fabrication in an ambient/dry air condition. (3) Chemical stability with the regular solvent and binder. This makes prelithiation materials compatible with current industrial battery fabrication processes. Electrochemical reversibility is not required, since we only need it to serve as a lithium source once to compensate the lithium loss in the first cycle. Currently, stabilized lithium metal powders^{11,14–16} and lithium silicide particles^{12,17} have been explored as anode prelithiation materials due to their high specific capacity and high prelithiation efficiency is achieved by using a small amount of such additives. Despite their high capacity, these anode prelithiation materials suffer from poor stability and compatibility with current industrial battery fabrication processes [such as slurry mixing using polyvinylidene fluoride (PVDF) binder and N-methyl-2-pyrrolidone (NMP) solvent] due to their low potential and active chemical reactivity. In this regard, cathode prelithiation materials, with

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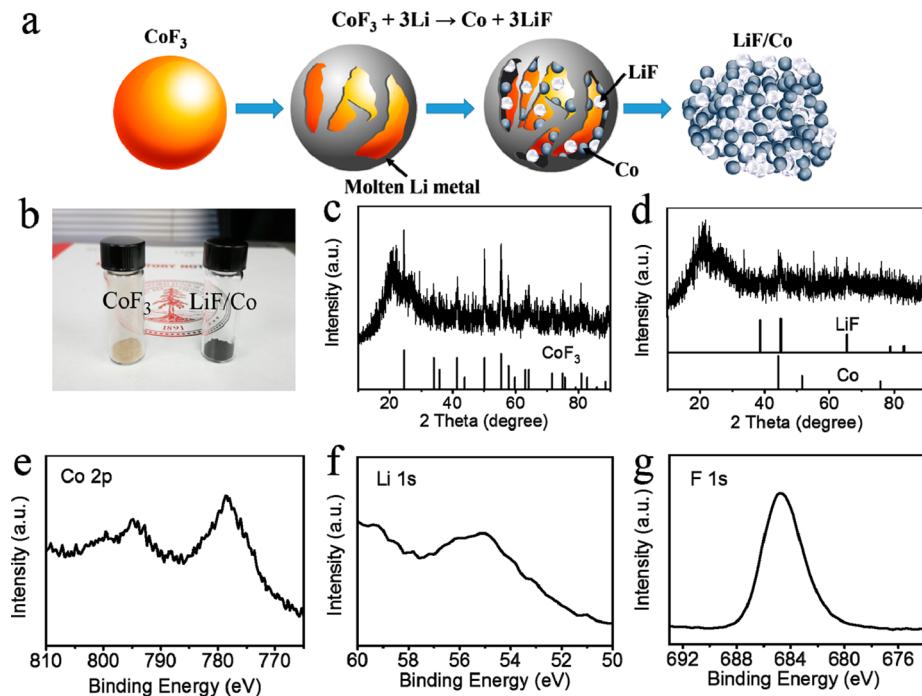


Figure 1. (a) Schematic of the formation process of the LiF/Co nanocomposite. (b) Digital images of the starting CoF₃ powder (left) and the LiF/Co product (right). XRD patterns of (c) the starting CoF₃ and (d) the LiF/Co product. High-resolution XPS spectra of (e) Co 2p, (f) Li 1s, and (g) F 1s. The XRD peaks at 21° and 27° arise from the Kapton tape.

relatively high open circuit voltage (OCV) and stability, allow greater flexibility in LIB applications. Nonetheless, considerably less attention has been paid to the exploration of cathode prelithiation materials.^{10,18} It is desirable to have stable cathode prelithiation materials with high first-cycle “donor” lithium-ion capacities (e.g., >400 mA h g⁻¹ or >1200 mAh cm⁻³) and good prelithiation efficiency. Most recently we have explored a conversion reaction based nanoscale mixture of Li₂O and metal as a cathode prelithiation material, which offers a high first-cycle “donor” lithium-ion specific capacity (e.g., 609 mA h g⁻¹ for the Li₂O/Co composite, 612 mA h g⁻¹ for the Li₂O/Fe composite, and 495 mA h g⁻¹ for the Li₂O/Ni composite).¹⁹ Here we would like to explore whether other lithium compounds can be effective as cathode prelithiation additives based on conversion reaction.

We propose that LiF can be a promising cathode prelithiation material due to its high lithium content and good stability in ambient atmosphere. However, LiF is a poor electronic and ionic conductor.²⁰ The electrochemical decomposition potential for pure LiF is 6.1 V (2LiF → 2Li⁺ + F₂ + 3e⁻),²¹ far higher than the cutoff potential of current cathode materials (usually <4.4 V). This makes it difficult to extract lithium during the cathode charge process. Additionally, the decomposition of LiF produces toxic fluorine gas. This situation is similar to that of the previously reported sacrificial lithium salt additives, which produce undesired gaseous N₂, CO or CO₂ accompanied by the lithium extraction.¹³ Therefore, despite the merits of LiF, it is challenging to overcome its intrinsic problems and achieve an efficient cathode prelithiation material.

In this work, we develop a unique approach to enable LiF as a superior cathode prelithiation material by constructing a metal-based nanocomposite. This nanocomposite enables a well-known mechanism of battery conversion reaction. The intrinsic problems that pure LiF faces, including low electronic conductivity, evolution of toxic fluorine gas, and high lithium

extraction potential, can be resolved. As a typical example, we show the synthesis of a LiF/Co nanocomposite with Co nanoparticles uniformly embedded in a LiF matrix via a simple chemical reaction process and its successful demonstration as a superior cathode prelithiation material for LIBs. It is important to note that the Co content in our LiF/Co nanocomposite is stoichiometric for the complete conversion reaction (Co + 3LiF → CoF₃ + 3Li⁺ + 3e⁻); thus, the nanocomposite still has a high theoretical specific capacity (683 mA h g⁻¹). In addition, although the lithium can be extracted from LiF/Co nanocomposite during the cathode charge process, the resulting CoF₃ would not be lithiated any further due to the large charge/discharge voltage hysteresis of conversion-reaction materials.^{21–23} Thus, a high “donor” lithium-ion capacity can be achieved. We note that, while the large voltage hysteresis is a disadvantage for conversion electrode materials, it is an advantage for the use of these materials as cathode prelithiation additives.

The LiF/Co nanocomposite was synthesized through the chemical reaction between molten lithium and CoF₃ powder in an inert atmosphere (Figure 1a, see details in Supporting Information, SI). Molten lithium metal and CoF₃ powder were mixed together under mechanical stirring at 240 °C with a molar ratio of 3:1 according to the conversion reaction equation (3Li + CoF₃ → Co + 3LiF). Liquid molten lithium metal has high chemical affinity and reaction activity with CoF₃. Once they come into contact, the liquid molten lithium starts to react with CoF₃ particles to form LiF and Co on the surface. This chemical reaction penetrates deep into the whole CoF₃ particle until all the lithium is consumed, and the initial CoF₃ particle converts to LiF/Co nanocomposite completely. After the reaction, the initial dark yellow powder turns into a black product (Figure 1b).

The X-ray diffraction (XRD) patterns for the starting CoF₃ and Co/LiF product are shown in Figure 1c and d, respectively.

The starting CoF_3 exhibits sharp XRD peaks with strong intensity, indicating its big particle size and high crystallinity (Figure 1c). After the reaction, the XRD peaks for CoF_3 (JCPDS no. 09–0033) disappear and new peaks are observed, suggesting the chemical reaction-induced phase change (Figure 1d). Clearly, these peaks can be readily indexed to mixed phases of Co (JCPDS no. 15–0806) and LiF (JCPDS no. 04–0857), in agreement with the product of the conversion-reaction equation. The significant broadening and reduced intensity of the XRD peaks confirm the nanocrystalline nature for the LiF/Co product. Despite the structure change, scanning electron microscopy (SEM) images show that the overall morphology of the starting CoF_3 is preserved after the reaction (Figure S1, SI). Further evidence of the LiF/Co composite is found by the X-ray photoelectron spectroscopy (XPS) investigation. The high-resolution Co 2p XPS spectrum indicates the presence of Co with Co 2p 1/2 at 793.7 eV and Co 2p 3/2 at 778.4 eV (Figure 1e).²⁴ The Li 1s peak is centered at 55.6 eV (Figure 1f), whereas the F 1s peak is found at 684.8 eV (Figure 1g), verifying the existence of LiF.^{25,26}

Transmission electron microscopy (TEM, Figure 2a) and scanning TEM (STEM, Figure 2b) images show that the LiF/

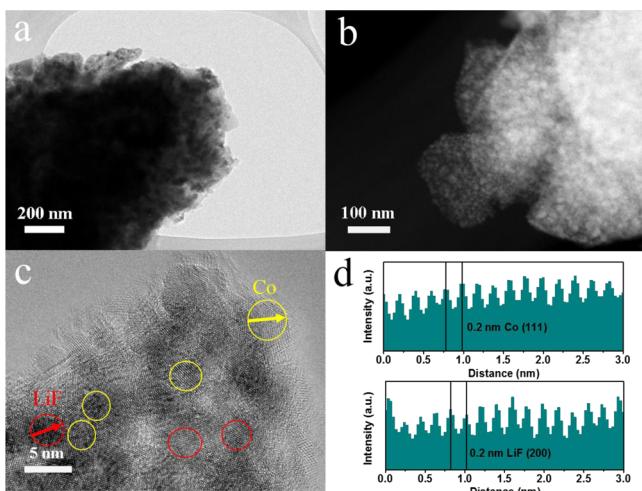


Figure 2. (a) TEM and (b) STEM images of the LiF/Co nanocomposite. (c) A HRTEM image and (d) the corresponding fringes of selected Co and LiF nanoparticles, showing their crystallinity and the small particle size. The HRTEM image shows two sets of equal lattice plane spacing of 0.20 nm with a plane angle of 60° for Co [111], and two sets of equal lattice plane spacing of 0.20 nm with a plane angle 90° for LiF [200].

Co composite has a unique nanostructure, where Co nanoparticles are uniformly embedded in a LiF matrix. The gray area in the STEM image is assigned to the LiF matrix, while the light patches suggest the existence of numerous Co nanoparticles with higher projected mass density. In the LiF/Co nanocomposite, the embedded Co nanoparticles enhance the electrical conductivity and the small dimension of LiF nanoparticles reduces the diffusion distance of lithium ions during their extraction process. Also, the Co nanoparticles make the nanocomposite electrically connected to the cathode during the first-cycle charge process. More importantly, the lithium exaction mechanism changes from the direct decomposition to a conversion reaction after the introduction of Co.²¹ This reduces the lithium-exaction potential within the cutoff voltage range of existing cathode materials and avoids the

production of toxic fluorine gas. A high-resolution TEM (HRTEM) image was shown in Figure 2c. Both the Co and LiF matrix are composed of nanoparticles. The nanocrystalline nature and an ultrafine crystallite size of Co and LiF nanoparticles (~ 5 nm) are confirmed. In comparison, the initial individual CoF_3 particles have dimensions ranging from 100 to 300 nm with high crystallinity (Figure S2, SI). A typical Co nanoparticle shows two sets of the lattices with an equal lattice plane spacing of 0.20 nm and a plane angle of 60°, corresponding to (111) and (−111) lattice planes of cubic Co. Two sets of lattices with an equal lattice plane spacing of 0.20 nm and angle of 90° are observed for a representative LiF nanoparticle, consistent with its (200) and (020) lattice planes. The lattice fringes of selected Co and LiF nanoparticles labeled in Figure 2c are shown in Figure 2d. The ability of extracting lithium from LiF/metal composites is related with the particle size and uniformity of the components.²¹ Due to the intimate nanoscale mixing of LiF and Co, as well as their small dimensions, the as-prepared nanostructure may deliver a high specific capacity during the first-cycle charge process in the cutoff potential range of existing cathodes.

Next, we investigated the first-cycle “donor” lithium-ion specific capacity and the prelithiation efficiency of the as-made LiF/Co nanocomposite. As shown in Figure 3a (left), the cutoff charge voltage of existing cathode materials is usually between 4.2–4.3 V vs Li^+/Li (e.g., 4.2 V for LiFePO_4 , 4.3 V for LiMnO_4 and LiCoO_2), while the cutoff discharge voltage in current cathodes is usually larger than 2.5 V (e.g., 2.5–3 V). Hence, an ideal cathode prelithiation material should release its “donor” lithium ions below 4.2 V in the first-cycle charge process and not be lithiated in the corresponding discharge process above 2.5 V, which requires a large potential hysteresis. The ideal delithiation and lithiation potential of the LiF/Co nanocomposite is illustrated in Figure 3a (right). Experimentally, a wide cutoff potential range of 4.2–0.7 V vs Li^+/Li and a low current density of 50 mA g^{−1} were applied to investigate the delithiation and lithiation electrochemical windows for the LiF/Co composite. The first-cycle galvanostatic charge/discharge profiles of a pristine LiF/Co electrode are shown in Figure 3b. The LiF/Co electrode has a reasonably high OCV of 1.5 V, which makes no negative effects on the stability of cathode materials. It is observed that its potential range for lithium extraction is 3.2–4.2 V. Its initial specific charge capacity reaches as high as 520 mA h g^{−1}, while the specific discharge capacity is only 4 mA h g^{−1} between 4.2–2.5 V, showing a high “donor” lithium-ion specific capacity of 516 mA h g^{−1}. The intake of amount of lithium happens below 2.2 V, which is lower than that of the cutoff discharge potential for existing cathodes (>2.5 V). These electrochemical characteristics meet the requirements of working potential and “donor” lithium-ion capacity as a superior cathode prelithiation material. Thus, when used as a cathode prelithiation additive, almost all the lithium in the LiF/Co nanocomposite can be extracted during the cathode charge process but does not transform back to the initial state during the discharge process. Previously during the study of using metal fluorides as battery electrodes (instead of prelithiation additives), high lithium-ion specific capacity was realized by electrochemical reversible formation and decomposition of LiF in a metal fluoride/lithium metal half cell via the conversion reaction $\text{MF}_n + n\text{Li}^+ + ne^- \leftrightarrow \text{M} + n\text{LiF}$. Because the electrochemically formed LiF/metal composite has an atomic level mixture which is kinetically favorable for the lithium extraction during the charge process.²¹ However, a high

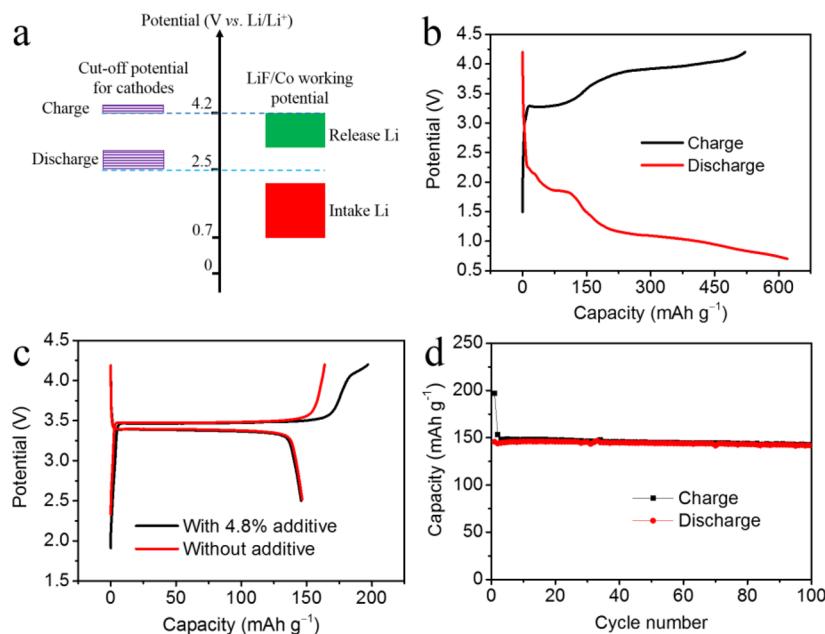


Figure 3. (a) Schematic illustration of the cutoff potential for existing cathodes (left) and the ideal delithiation and lithiation potential for LiF/Co nanocomposite (right). (b) The initial charge and discharge curves for the LiF/Co electrode within the potential range of 4.2–0.7 V vs Li⁺/Li at the current density of 50 mA g⁻¹. (c) The comparison of the first-cycle charge and discharge curves of LiFePO₄ electrodes versus lithium metal in half cells with and without LiF/Co additive within the potential range of 4.2–2.5 V vs Li⁺/Li at 0.1 C. (d) Cycling stability for the LiFePO₄ electrode with 4.8% LiF/Co additive.

charge specific capacity has not been thus far achieved yet for a nonelectrochemically produced LiF/metal composite due to the difficulty in achieving thorough mixing of metal and LiF particles via regular material preparation methods.²⁷ In this respect, we highlight the success of our LiF/Co nanocomposite as an effective structure design for the lithium extraction. Compared with the electrochemically formed LiF/Co composites, the lithium-extraction potential and OCV of the chemically synthesized LiF/Co composite increase (Figure S3, SI), arising from the slightly increased particle size,²¹ which makes electrodes stable during their processing. It is noteworthy that the electrode fabrication processes were all carried out in regular slurry processing using PVDF binder in NMP solvent in an ambient condition. Therefore, the achieved LiF/Co nanocomposite possesses all the required characteristics for a good cathode prelithiation additive: high “donor” lithium-ion capacity, high stability, and good compatibility with the regular solvent, binder, and industrial battery fabrication processes such as slurry making and electrode baking.

To further evaluate its electrochemical compatibility with cathode materials and lithium compensation effect, the LiF/Co nanocomposite was used as a prelithiation additive to the commercial LiFePO₄ cathode material and the galvanostatic charge/discharge measurement of the composite electrode was carried out versus lithium metal counter/reference electrodes in half cells. Compared with the pristine LiFePO₄ electrode, the LiFePO₄ electrode with 4.8 wt % LiF/Co additive exhibits an obvious voltage slope above the charge plateau of the pristine LiFePO₄, arising from the lithium extraction process from the additive (Figure 3c). As predicted, the LiFePO₄ electrode with 4.8 wt % LiF/Co additive indeed delivers an increased initial charge specific capacity of 197 mA h g⁻¹ at 0.1 C, which is 33 mA h g⁻¹ (or 20.1%) higher than that (164 mA h g⁻¹) of the pristine LiFePO₄ electrode based on the mass of LiFePO₄ (Figure 3c). This discharge capacity is very similar (145.9 and

146.6 mA h g⁻¹ with and without prelithiation, respectively). When calculated based the total mass of the additive and LiFePO₄, the initial charge specific capacity of the cathode is 185 mA h g⁻¹, still higher than 164 mA h g⁻¹ for the pristine LiFePO₄ electrode. The increased lithium-ion charge specific capacity can be used as the additional lithium source to compensate the lithium loss in full cells and increase the overall mass energy density of LIBs. Moreover, the hybrid electrode shows stable cyclability, verifying that the LiF/Co nanocomposite does not have any negative effect on the cathode materials (Figure 3d and Figure S4, SI).

To show the generality of preparing the conversion-reaction based LiF/metal nanocomposites and their applications as efficient cathode prelithiation materials, we also synthesized LiF/Fe nanocomposite with the same procedure according to the reaction equation: FeF₃ + 3Li → Fe + 3LiF. XRD results confirm that LiF/Fe nanocomposite has been prepared after the chemical transformation reaction between FeF₃ and lithium metal (Figures S5–6, SI). The color turns from pale for the initial FeF₃ to black for the LiF/Fe nanocomposite (Figure S7). TEM and STEM results indicate Fe nanoparticles are embedded in the LiF matrix uniformly, and both the Fe and LiF particles are ranging from 5 to 10 nm (Figure 4a). Figure 4b displays the voltage profiles of the as-synthesized LiF/Fe nanocomposite for the first cycle. As expected, the LiF/Fe nanocomposite exhibits a high OCV of 1.8 V. The first-cycle charge specific capacity reaches 565 mA h g⁻¹ with a cutoff charge potential of 4.5 V, indicating most of the lithium in the LiF/Fe composite is extracted. Below the cutoff charge potential of existing cathodes (4.3 V), a high capacity of 532 mA h g⁻¹ is still achieved. Meanwhile, the LiF/Fe nanocomposite delivers a negligible discharge specific capacity of 26 mA h g⁻¹ with the cutoff discharge potential of 2.5 V. Thus, a high donor lithium-ion capacity (506 mA h g⁻¹) is obtained for

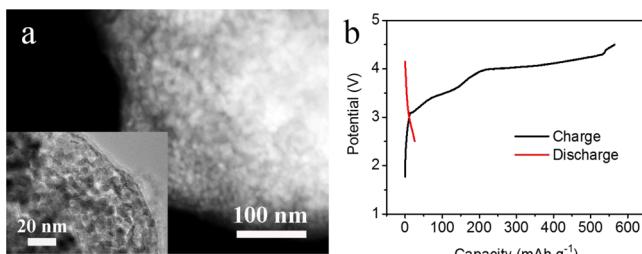


Figure 4. (a) STEM and high-magnification TEM images (inset of part a) of the LiF/Fe nanocomposite and (b) the initial charge and discharge curves for the pristine LiF/Fe electrode with the potential range of 4.5–2.5 V vs Li⁺/Li at the current density of 50 mA g⁻¹. The STEM image shows that Fe particles are uniformly embedded in the LiF matrix. The TEM image at high magnification indicates that the particle size of the LiF and Fe nanodomains is 5–10 nm.

the as-prepared LiF/Fe nanocomposite within the potential range of existing cathodes.

In summary, a LiF/Co nanocomposite has been successfully synthesized through a facile one-step chemical reaction process between molten lithium metal and CoF₃. The nanoscale mixing of LiF and Co and their small particle size (~5 nm) render the easy electrochemical extraction of lithium from the achieved LiF/Co nanocomposite via an inverse conversion reaction during the cathode charge process, while its lithiation process does not happen during the cathode discharge process due to the large voltage hysteresis, which leads to a high “donor” lithium-ion capacity. The pristine LiF/Co electrode delivers a high charge capability of 520 mA h g⁻¹ and a low discharge capacity of 4 mA h g⁻¹. LiFePO₄ cathode with 4.8% LiF/Co additive shows increased first-cycle charge capacity, ~20% higher than the pristine LiFePO₄ counterpart, indicating high prelithiation efficiency. The facile synthesis, high “donor” lithium-ion capacity, and good stability in ambient and battery processing conditions make the LiF/Co nanocomposite an ideal cathode prelithiation material to compensate the first-cycle lithium loss in current LIBs and boost next-generation LIBs involving anode materials with larger initial lithium loss (e.g., Si and Sn). In addition, the LiF/Fe nanocomposite was also prepared for high capacity prelithiation of cathodes using the same synthesis route. We believe that the concept of nanoscale mixing of LiF with other metals (for example, other first row transition metals such as Ti, V, Mn, Ni, Cu, Zn, and main group elements such as Al, Sn) can also work as prelithiation additive since their electrochemical conversion reaction has been shown.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.nanolett.5b05228](https://doi.org/10.1021/acs.nanolett.5b05228).

Experimental details and additional characterizations ([PDF](#))

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Notes

The authors declare no competing financial interest.

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