

High-capacity battery cathode prelithiation to offset initial lithium loss

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Loss of lithium in the initial cycles appreciably reduces the energy density of lithium-ion batteries. Anode prelithiation is a common approach to address the problem, although it faces the issues of high chemical reactivity and instability in ambient and battery processing conditions. Here we report a facile cathode prelithiation method that offers high prelithiation efficacy and good compatibility with existing lithium-ion battery technologies. We fabricate cathode additives consisting of nanoscale mixtures of transition metals and lithium oxide that are obtained by conversion reactions of metal oxide and lithium. These nanocomposites afford a high theoretical prelithiation capacity (typically up to 800 mAh g⁻¹, 2,700 mAh cm⁻³) during charging. We demonstrate that in a full-cell configuration, the LiFePO₄ electrode with a 4.8% Co/Li₂O additive shows 11% higher overall capacity than that of the pristine LiFePO₄ electrode. The use of the cathode additives provides an effective route to compensate the large initial lithium loss of high-capacity anode materials and improves the electrochemical performance of existing lithium-ion batteries.

Rechargeable lithium (Li)-ion batteries at present dominate the portable electronics market and exhibit great potential for electric vehicles, grid-scale energy storage and renewable energy storage^{1–5}. Commercial Li-ion batteries are composed of two electrodes: an intercalated lithium transition metal oxide cathode (for example, LiCoO₂, LiMn₂O₄ and LiFePO₄) and a graphite anode. During the first charge process, 5–20% of the Li from the cathode is usually consumed owing to the solid electrolyte interphase (SEI) formation at the anode surface, leading to low first-cycle Coulombic efficiency and a high initial irreversible capacity loss^{6–12}. Electrochemical prelithiation routes, such as directly placing a Sn–C electrode in direct contact with a Li foil wetted by the electrolyte solution¹³ and discharging a Si nanowire electrode/Li foil half cell¹⁴, showed effective Li compensation efficiency. In spite of their success, such complex operation processes and their instability in ambient atmosphere were not suitable for scale-up. Another method to compensate the first-cycle Li loss is to load additional cathode materials. However, owing to the low specific capacity (<200 mAh g⁻¹) of existing cathode materials, a large amount of additional loading is needed, which reduces appreciably the specific energy and energy density of the entire battery. This challenge calls for specifically designed prelithiation additives as high-specific-capacity Li donors to offset the initial Li loss. Some progress has been made in the design of such prelithiation materials on both anodes and cathodes. Stabilized Li metal powders and Li silicide nanoparticles were added to the anodes for prelithiation^{15–17}. The irreversible capacity of the anodes can be compensated by a small amount of such additives. However, anode prelithiation materials have a low potential and high chemical reactivity, creating compatibility issues with ambient environments, common solvents, binders and thermal processing in Li-ion batteries. Cathode prelithiation is another route to compensate the Li loss in the battery (Supplementary Fig. 1). Sacrificial Li salt additives (for example, azide, oxocarbons, dicarboxylates and hydrazides) exhibited Li compensation effects for the first irreversible capacity loss. However, as mentioned in ref. 18, the use of these additives was accompanied

by the evolution of undesired gaseous N₂, CO or CO₂. Similarly, Na₃N was used as an additive in sodium-ion batteries with concomitant N₂ evolution¹⁹. Moreover, some earlier work on Li-rich compounds as cathode additives (for example, Li₂NiO₂ and Li₆CoO₄) has been carried out^{20,21}. In spite of the progress, the effective compensation of the first-cycle Li loss is still limited by their low specific capacity (~300 mAh g⁻¹). In this work, we develop a one-pot chemical reaction route to synthesize nanocomposites of lithium oxide (Li₂O) and metal (M) with deep nanoscale mixing for battery cathode prelithiation. Owing to the unique characteristics of the large potential hysteresis of the conversion reaction, the lithium in such nanocomposites can be easily extracted on charging, whereas it does not transform back to the initial state on discharging. Therefore, the as-synthesized M/Li₂O nanocomposites deliver a high 'donor' Li-ion capacity. As an example, we show that the overall capacity of a LiFePO₄ cathode with the Co/Li₂O additive is appreciably improved in a full-cell configuration.

Design for cathode prelithiation

To search for an effective cathode prelithiation additive, we believe that the following points can serve as good guidelines. First, a good cathode additive should possess a much higher Li storage capacity by weight and volume than the existing cathode materials. For example, if we choose doubling of the existing cathode materials as a criterion, we would need to find a prelithiation additive with capacity >400 mAh g⁻¹ or >1,200 mAh cm⁻³. Second, the additive should be able to release its stored Li ions below the maximum potential during cathode charge, but not take in Li ions at the minimum potential of cathode discharge (Fig. 1a). That is, we would need the delithiation potential of additives to be below the maximum cathode charge potential while the lithiation potential of additives should be below the minimum cathode discharge potential. This implies that the delithiation/lithiation potential curve of additives should have a large hysteresis. Third, the cathode prelithiation additives should not have intolerable negative effects on the stability of electrode materials, electrolyte, and the whole battery. Usually, that means

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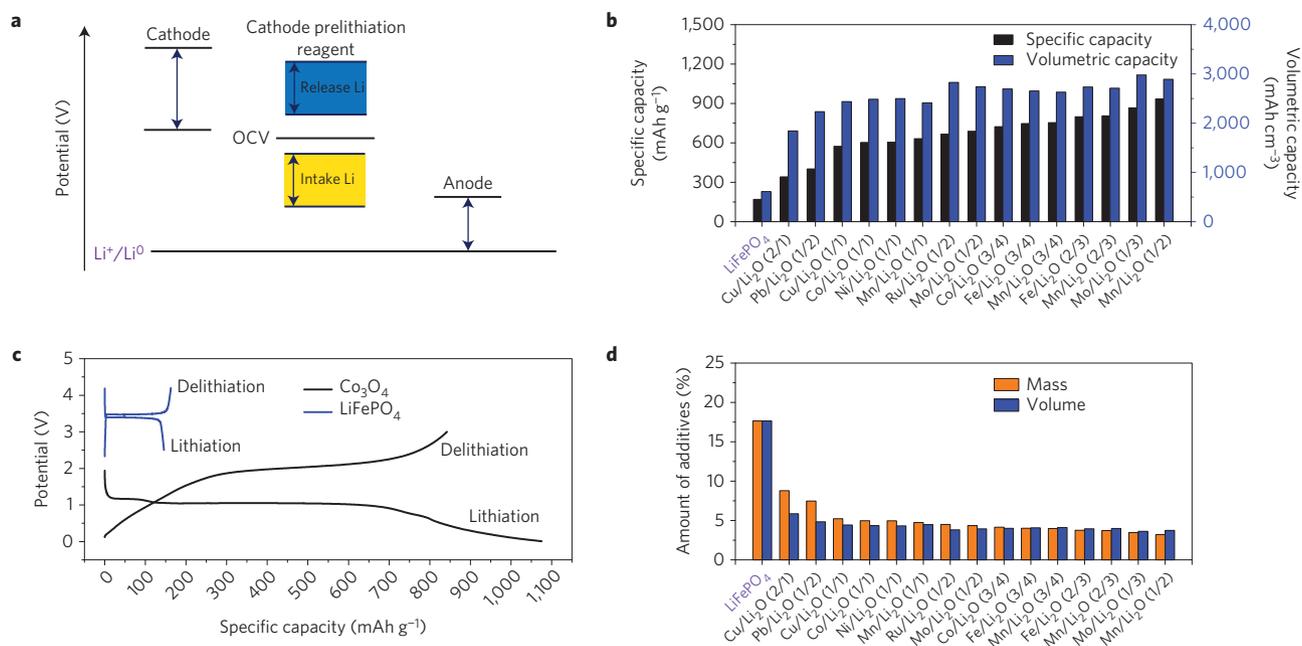


Figure 1 | Schematic of M/Li₂O composite cathode additives for a Li-ion battery. **a**, Potential requirement for ideal cathode additives: complete delithiation below the cutoff charge potential of the cathodes and starting lithiation below their cutoff discharge potential. **b**, Theoretical specific capacities and volumetric capacities of various M/Li₂O composites based on the inverse conversion reaction. **c**, Typical potential curves of MOs (for example, Co₃O₄) and existing commercial cathodes (for example, LiFePO₄). The Li in M/Li₂O composites can be extracted below the cutoff charge potential of the cathodes but not consumed by MOs above their cutoff discharge potential. **d**, Required amount of M/Li₂O cathode prelithiation materials to achieve complete Li compensation in comparison to that using an extra amount of cathode material (in the case of a LiFePO₄/graphite full cell with an initial irreversible Li loss of 30 mAh g⁻¹).

a relatively high open-circuit voltage (OCV) is needed (Fig. 1a). Fourth, the cathode prelithiation additives should ideally be stable in ambient conditions and compatible with existing industrial battery fabrication processes such as slurry mixing, coating and baking.

With the above criteria in mind, we identify the reaction products of transition metal oxides (MOs) with Li to be excellent candidates as cathode prelithiation additives. The MOs (M_xO_y, M = Fe, Co, Ni, Mn, and so on) have been intensively investigated as potential anode materials over the past decade^{22–27}. They can react with Li through a conversion-reaction mechanism (M_xO_y + 2yLi⁺ + 2ye⁻ → xM + yLi₂O) to form nanocomposites of M and Li₂O. The M/Li₂O nanocomposites store more than four times the theoretical specific capacity of existing cathodes (for example, 724 mAh g⁻¹ for Co/Li₂O (molar ratio, 3/4), 799 mAh g⁻¹ for Fe/Li₂O (molar ratio, 2/3), and 935 mAh g⁻¹ for Mn/Li₂O (molar ratio, 1/2), see Fig. 1b and Supplementary Table 1). On the basis of the density of M and Li₂O, they can also deliver high volumetric capacities (for example, 2,695 mAh cm⁻³ for Co/Li₂O (molar ratio, 3/4), 2,735 mAh cm⁻³ for Fe/Li₂O (molar ratio, 2/3) and 2,891 mAh cm⁻³ for Mn/Li₂O (molar ratio, 1/2), see Fig. 1b and Supplementary Table 1).

The conversion reactions of MOs usually exhibit a lithiation potential below 1.2 V and a near complete delithiation at a potential below ~3 V, which show a large charge/discharge voltage hysteresis. For example, Fig. 1c shows the experimental first-cycle electrochemical lithiation/delithiation voltage curve of Co₃O₄, where lithiation mainly takes place between 1.2 to 0.01 V and delithiation can provide a very high Li-ion capacity of 842 mAh g⁻¹ below 3 V. The wide voltage range and large hysteresis make conversion oxides alone not ideal either as good anode or cathode materials^{28,29}. However, these very characteristics of conversion oxides make them excellent prelithiation additives for cathodes. The charge cutoff potential of existing cathode materials is usually larger than 4.0 V versus Li/Li⁺ (for example, 4.2 V for LiFePO₄ and 4.3 V for LiCoO₂, Fig. 1c), which is high enough to easily

extract the Li from the M/Li₂O composites. Meanwhile, their discharge cutoff potential is higher than 2.5 V (for example, 2.5 V for LiFePO₄ and 3.0 V for LiCoO₂, Fig. 1c), which is still much higher than the lithiation potential of MOs. In other words, M/Li₂O composites as cathode additives can contribute a large amount of Li during the first charge process of cathodes, whereas their lithiation reaction cannot occur in the cathode discharge process. The impact of having M/Li₂O composites as prelithiation additives is shown in Fig. 1d, which shows the amount of additional material needed to compensate the first-cycle Li loss (for example, 30 mAh g⁻¹) in a LiFePO₄/graphite full cell. One has to load an additional 18% of LiFePO₄ cathode material. In contrast, only 3–5% of M/Li₂O cathode additives is needed to offset this initial Li loss (Fig. 1d). Correspondingly, the specific and volumetric energy densities are increased to 8–13% and 11–14%, respectively (Supplementary Fig. 2).

Electrochemistry of the Co/Li₂O nanocomposite

The above promising analysis on using M/Li₂O composites as cathode prelithiation additives has motivated us to experimentally demonstrate such a possibility and uncover the unknowns related to this novel concept. In this work, we develop a general one-step synthesis method for M/Li₂O (M: Co, Fe, Ni, *et al.*) nanocomposites (Fig. 2a) and demonstrate their successful application as cathode additives to effectively compensate the Li loss during the first charge process in Li-ion batteries. A nanometre-sized metal/nanometre-sized lithium oxide (N-M/N-Li₂O) composite was synthesized by mixing M_xO_y with molten Li under Ar atmosphere. The molar ratio of the starting M_xO_y and Li was set according to the conversion-reaction equation (M_xO_y + 2yLi → xM + yLi₂O). Li metal foil was melted at 185 °C and reacted with M_xO_y for 20 min under mechanical stirring. Then, the temperature was further increased to 200 °C and kept for 2 h for their complete reaction. Finally, a uniform nanocomposite comprising nanometre-sized

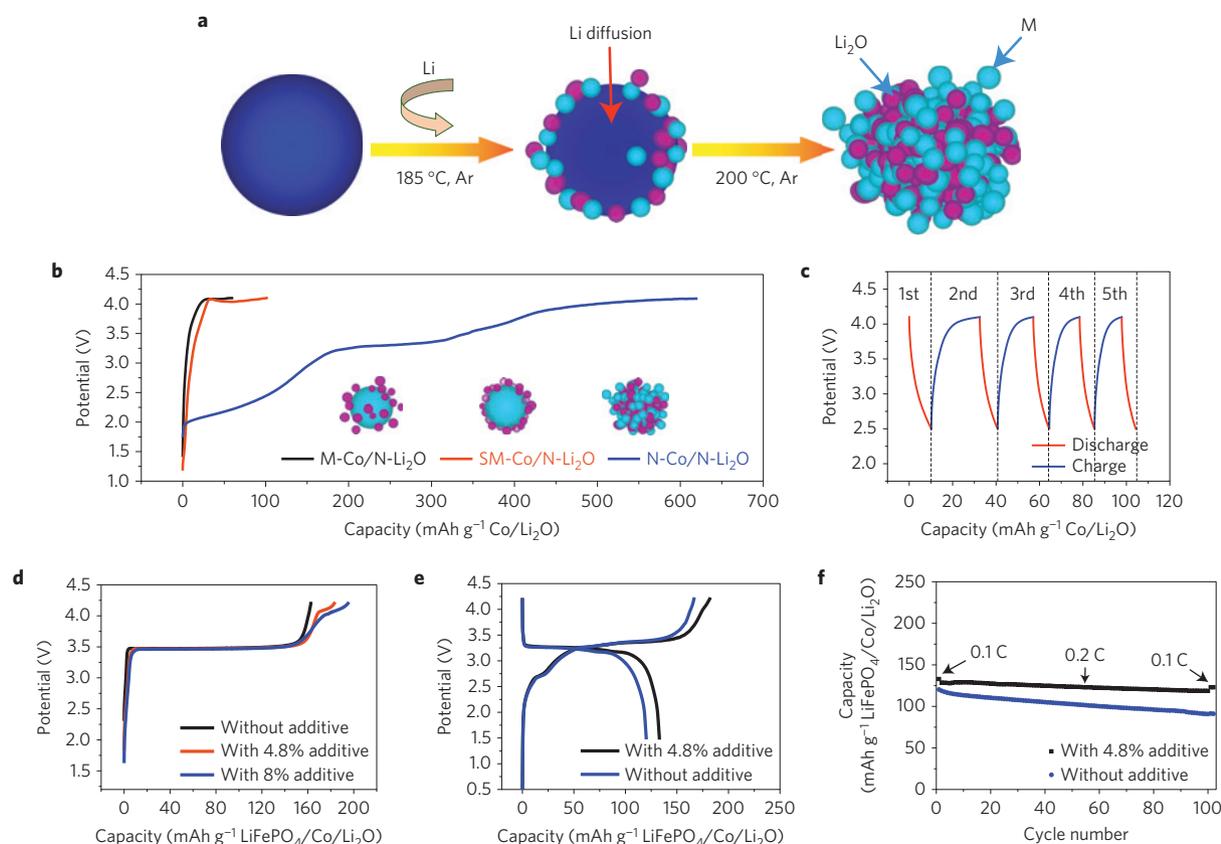


Figure 2 | Fabrication and electrochemical characteristics of the N-Co/N-Li₂O composite. **a**, Schematic of the fabrication process of the N-M/N-Li₂O composites. MOs are used as the starting materials and *in situ* converted into N-M/N-Li₂O composites through the chemical reaction with molten Li. **b**, Initial charge potential profiles of the electrodes made with various Co/Li₂O nanocomposites: M-Co/N-Li₂O composite, SM-Co/N-Li₂O composite and N-Co/N-Li₂O composite. **c**, Charge/discharge potential profiles of the N-Co/N-Li₂O electrode after the first charge process. **d**, Initial charge potential profiles of LiFePO₄ electrodes with different amounts of the N-Co/N-Li₂O additive in half-cell configurations. **e, f**, The initial charge/discharge potential profiles (**e**) and cycling performance (**f**) of LiFePO₄/graphite full cells with and without the N-Co/N-Li₂O additive. The specific capacities of the cathodes are evaluated on the basis of the weight of LiFePO₄ and the N-Co/N-Li₂O additive.

metal particles embedded in a nanometre-sized Li₂O matrix was obtained (Fig. 2a). These M/Li₂O nanocomposites are used in regular slurry processing in ambient conditions to form battery electrodes (see Methods).

As a typical example, the electrochemical performances of the nanometre-sized Co/nanometre-sized Li₂O (N-Co/N-Li₂O; molar ratio, 3/4) composite were investigated (Fig. 2b,c). As expected, the as-prepared N-Co/N-Li₂O composite delivered a high charge specific capacity of 619 mAh g⁻¹ and a low discharge specific capacity of 10 mAh g⁻¹ for the first cycle in the potential range between 4.1 and 2.5 V, meeting the voltage criterion as a cathode prelithiation additive. For comparison, the electrochemical properties of two other Co/Li₂O nanocomposites, including micrometre-sized Co/nanometre-sized Li₂O (M-Co/N-Li₂O) and sub-micrometre-sized Co/nanometre-sized Li₂O (SM-Co/N-Li₂O) composites were also investigated (Fig. 2b). They exhibited a much higher charge potential (~4.1 V) and a lower specific charge capacity (<100 mAh g⁻¹), owing to the large particle size of Co and the loose contact between the Li₂O and Co particles (discussed later). These results highlight the importance of having thorough nanoscale mixing of Co and Li₂O. Note that slurry coating and electrode baking of the M-Co/N-Li₂O composite were carried out in ambient conditions. The Li-extraction specific capacity was 568 mAh g⁻¹ after an eight-hour exposure to ambient atmosphere, only 51 mAh g⁻¹ lower than the initial value. Even after two days, the Li-extraction specific capacity still reached 418 mAh g⁻¹, suggesting compatibility

with the conventional Li-ion battery fabrication environment (Supplementary Fig. 3).

The Li-extraction potential of the N-Co/N-Li₂O composite made by the one-step chemical reaction (Fig. 2b) is slightly higher than that produced by the electrochemical lithiation product of Co₃O₄ (Fig. 1c). This might result from the different grain sizes of Co/Li₂O nanocomposites produced by these two methods. In contrast to the counterpart produced by electrochemical lithiation (Fig. 1c), the chemically synthesized N-Co/N-Li₂O composite exhibits a high OCV of 1.8 V (Fig. 2b), which is high enough to be in the stability range of existing cathode materials. Thus it can be easily mixed with various cathode materials with negligible negative effects on their chemical and structural stability during electrode processing. Moreover, the N-Co/N-Li₂O electrode lost nearly all its capacity after the first cycle, suggesting that after providing Li ions during the first charge, these nanocomposites did not contribute to the active electrochemical process in the cathode (Fig. 2c). All these characteristics enable the N-Co/N-Li₂O cathode additive to effectively compensate for the first-cycle capacity loss in existing Li-ion batteries.

Figure 2d shows the charge potential profiles of LiFePO₄ cathode and Li metal anode half cells with different amounts of the N-Co/N-Li₂O cathode prelithiation material. Here, the specific capacity was calculated on the basis of the total weight of LiFePO₄ and the N-Co/N-Li₂O composite unless otherwise stated. The electrode made of pristine commercial LiFePO₄ powder delivers an initial charge capacity of 164 mAh g⁻¹. With a 4.8% N-Co/N-Li₂O additive (based on the entire cathode), the first-cycle

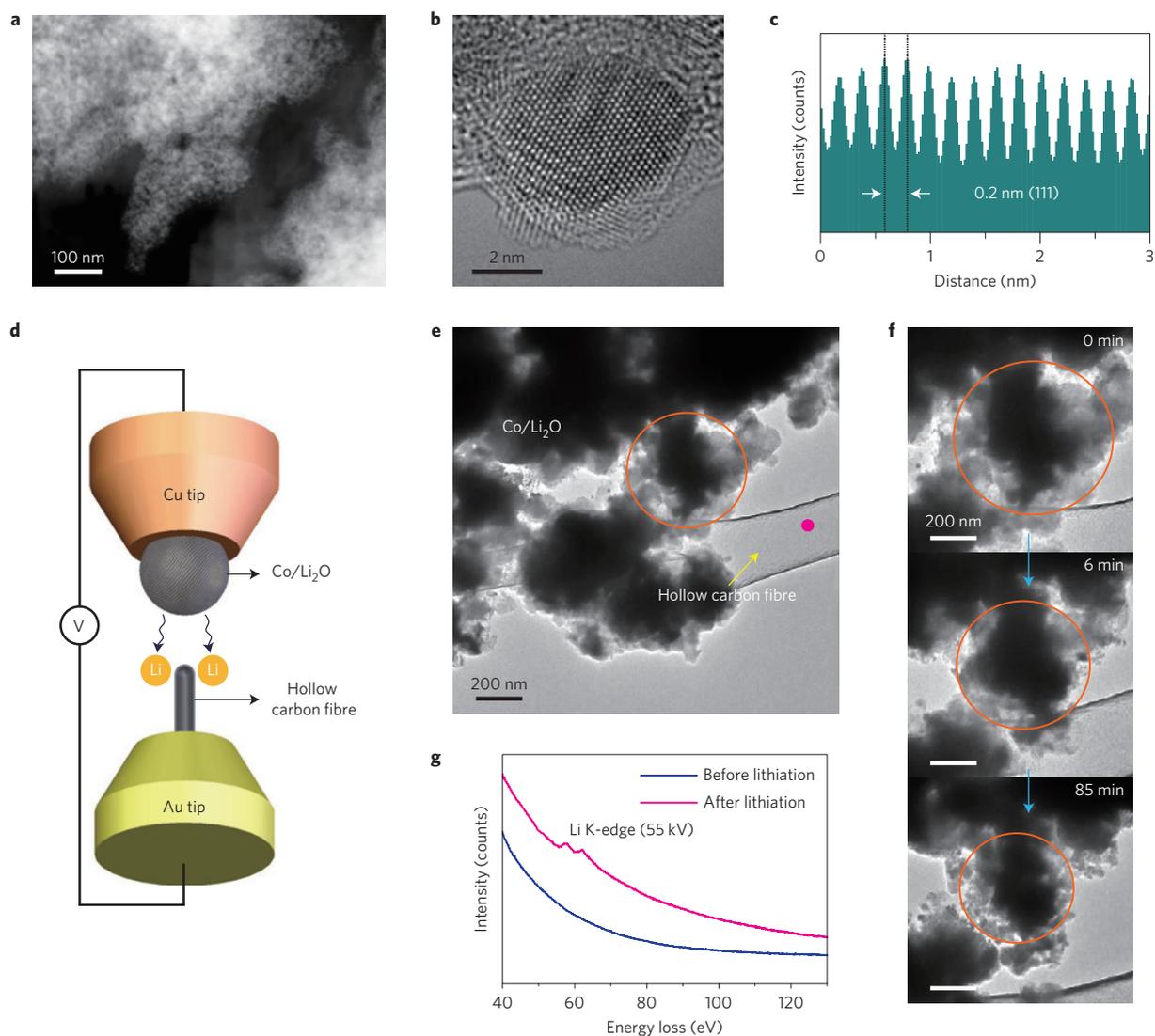


Figure 3 | Structure and evolution of the N-Co/N-Li₂O composite on the Li-extraction process. **a**, STEM image of the N-Co/N-Li₂O composite, showing that Co nanoparticles are uniformly embedded in a Li₂O matrix. **b,c**, HRTEM image (**b**) and the corresponding fringes (**c**) of a Co particle, showing its crystallinity and the small particle size. **d,e**, Schematic illustration (**d**) and configuration (**e**) of the *in situ* TEM device. The N-Co/N-Li₂O composite on a Cu tip serves as the working electrode and a template-fabricated hollow carbon fibre functions as the counter electrode. **f,g**, Time-lapse TEM images (**f**) and EELS spectra (**g**). After the voltage bias application, Li is extracted from the N-Co/N-Li₂O working electrode and transfers to the carbon counter electrode, leading to volume shrinkage. An N-Co/N-Li₂O particle aggregate is labelled by a red circle and its shrinkage in volume is observed. EELS spectra are taken at the hollow carbon fibre, labelled by a pink point in **e**, before and after the delithiation of the N-Co/N-Li₂O composite. The results indicate the transfer of Li from the working electrode to the counter electrode.

specific charge capacity reaches 183 mAh g⁻¹ (12% higher). When an 8% N-Co/N-Li₂O additive is used, the initial specific charge capacity is as high as 195 mAh g⁻¹ (19% higher). A potential slope above the charge plateau of the pristine LiFePO₄ is clearly observed, which is consistent with the delithiation process of the pristine N-Co/N-Li₂O composite (Fig. 2b,d). The response of the additive at different potential ranges is clearly shown by a LiFePO₄ electrode containing a large amount of the N-Co/N-Li₂O additive (with the additive/LiFePO₄ ratio of 1/6 in weight, Supplementary Fig. 4). Meanwhile, the LiFePO₄ cathodes with and without the N-Co/N-Li₂O additive in the Li metal half cells show high specific discharge capacities and stable cycling performance (Supplementary Fig. 5), indicating that the N-Co/N-Li₂O additive has negligible negative effects on the stability of the cathode during cycling. Anodes with prelithiation materials can form better passivating surface films on their surfaces than that of the pristine anodes, which may help achieve stable electrochemical performance

for the anodes¹⁶. A recent paper reported that a stable surface film on the LiNi_{0.5}Mn_{0.3}Co_{0.2}O₂ cathode surface could also be formed by cathode prelithiation activation, which improved the cycling stability of the LiNi_{0.5}Mn_{0.3}Co_{0.2}O₂ cathode³⁰. To show the generality of using the N-Co/N-Li₂O additive, we have also tried LiCoO₂ and LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ cathodes with such an additive to demonstrate its Li 'donor' effect. The first charge potential profiles of LiCoO₂ and LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ with and without the N-Co/N-Li₂O additive are shown in Supplementary Fig. 6. The Li 'donor' effect of the additive is clearly confirmed by the variations in potential slope caused by the additives and the increased overall capacities (based on the mass of cathode material and additive). The initial charge capacity for the LiCoO₂ electrode with a 4.8% N-Co/N-Li₂O additive is 190.8 mAh g⁻¹ (12% higher than 170.2 mAh g⁻¹ for the pristine LiCoO₂ electrode). With a 4.8% N-Co/N-Li₂O additive, the first-cycle specific charge capacity of the LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ cathode reaches 208.0 mAh g⁻¹ (9% higher than that of the pristine

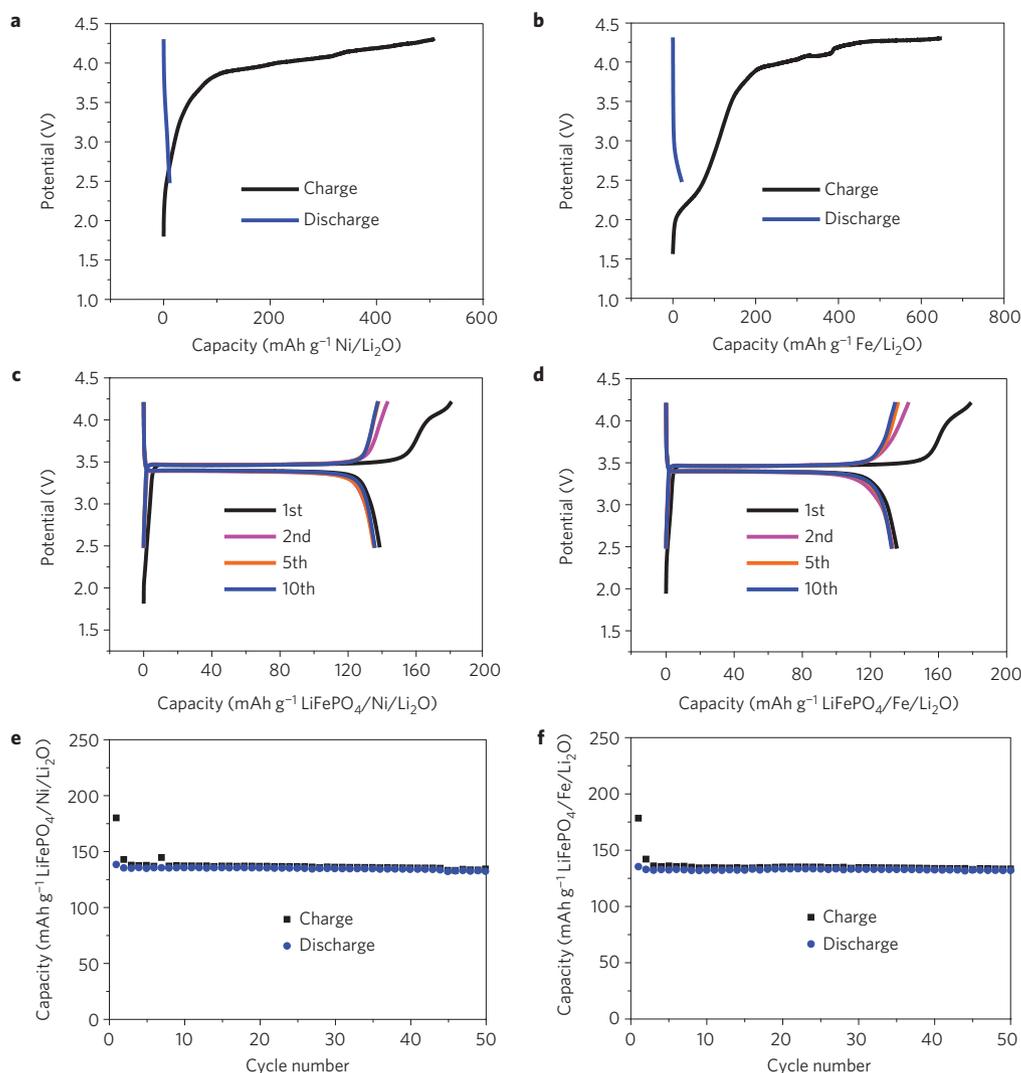


Figure 4 | Generalization to other N-M/N-Li₂O composites. **a,b**, Initial charge/discharge potential profiles of the pristine N-Ni/N-Li₂O (**a**) and N-Fe/N-Li₂O electrodes (**b**). **c,d**, Discharge/charge potential profiles of LiFePO₄ electrodes with 4.8% N-Ni/N-Li₂O (**c**) and N-Fe/N-Li₂O (**d**) additives in half-cell configurations. **e,f**, Cycling performance of LiFePO₄ electrodes with 4.8% N-Ni/N-Li₂O (**e**) and N-Fe/N-Li₂O (**f**) additives. The specific capacities of the cathodes are evaluated on the basis of the weight of LiFePO₄ and the additives.

LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ electrode). The electrodes with and without the additive show similar cycling stability, indicating that the N-Co/N-Li₂O additive has negligible negative effects on the stability of various cathodes.

In a full cell, all the Li comes from the cathode materials. Owing to the irreversible reaction during the first-cycle charge process, a certain amount of Li cannot go back to the cathode during the discharge process, which reduces the specific energy and energy density of a battery. Ideally, when the amount of cathode additive is optimized, the discharge capacity of the cathode in a full cell can reach the same value as that obtained in a Li metal half cell. To further evaluate the Li compensation effect of the N-Co/N-Li₂O composite, electrochemical characterizations of LiFePO₄/graphite full cells were carried out. As shown in Fig. 2e, the reversible discharge capacity of the as-made pristine LiFePO₄/graphite full cell without the N-Co/N-Li₂O cathode additive is only 120 mAh g⁻¹. In comparison, a LiFePO₄/graphite full cell with a 4.8 wt% N-Co/N-Li₂O cathode additive in the total cathode delivers a reversible discharge capacity of 133 mAh g⁻¹ (11% higher), on the basis of the weight of LiFePO₄ and the N-Co/N-Li₂O composite, which is the same value as that achieved in a LiFePO₄/Li metal half cell (Supplementary Fig. 5). When calculated on the basis of the weight of

LiFePO₄, the reversible discharge capacity is as high as 141 mAh g⁻¹ (Supplementary Fig. 7). The first-cycle charge potential profiles of the LiFePO₄/graphite full cell with and without the N-Co/N-Li₂O additive coincide well at a low charge potential (≤ 3.3 V), and a prolonged charge plateau and slope are observed for the cell with the Co/Li₂O cathode additive at a high charge potential (≥ 3.3 V). Correspondingly, the cell with the cathode additive shows a prolonged plateau during their discharge progress. These results confirm that the first-cycle capacity loss of a full cell is effectively compensated by the released capacity from the N-Co/N-Li₂O additive. The overall capacity and energy density of the entire Li-ion battery are appreciably improved. Furthermore, the full cell with a 4.8% cathode additive exhibits stable potential curves on cycling and significantly enhanced capacity retention with a small average capacity decay of 0.07% per cycle in 100 cycles (Fig. 2f and Supplementary Fig. 8), which has comparable or better stability than the reference pristine LiFePO₄/graphite full cell without the N-Co/N-Li₂O additive.

Structure characterizations and *in situ* TEM measurement

Next, we sought to investigate the structure of the N-Co/N-Li₂O composite and its evolution during the electrochemical Li-extraction process. Results from X-ray photoelectron spectroscopy

(XPS), electron energy loss spectroscopy (EELS) and X-ray diffraction (XRD) indicate the crystalline nature of Co nanoparticles and amorphous structure of Li_2O in the product (Supplementary Figs 9–11). The starting Co_3O_4 comprises micrometre-sized secondary particle aggregates with initial particle sizes of 50–100 nm (Supplementary Fig. 12). After the chemical reaction with Li, the microstructure changes significantly, although its overall shape is preserved (Supplementary Fig. 13). Transmission electron microscopy (TEM) results show that the starting particles are completely converted into ~ 5 nm Co nanoparticles embedded in a Li_2O matrix after the reaction (Supplementary Fig. 14). To gain insight into the distribution of metallic Co particles and Li_2O in the composite, scanning TEM (STEM) was carried out. As shown in Fig. 3a, a dark/light contrast in the STEM image is clearly observed. The grey area can be assigned to Li_2O . The light patches suggest the existence of numerous Co nanoparticles. It is worth noting that the metallic Co nanocrystals are uniformly embedded in the Li_2O matrix. The crystallinity of metallic Co is confirmed by high-resolution TEM (HRTEM) (Fig. 3b,c). Meanwhile, the uniform distribution of Li_2O and Co in the composite is verified by STEM/energy-dispersive X-ray spectroscopy (EDX) and STEM/EELS element mapping analysis (Supplementary Fig. 15). We believe that the small size of the Co particles and their uniform distribution in Li_2O , as well as the intimate contact between Co and Li_2O , are vital for the full electrochemical extraction of Li from the N-Co/N- Li_2O composite. The electrochemical activity of the conversion-reaction composites is influenced strongly by the microstructure and particle size. The composites with large particle sizes show higher Li-extraction potentials and lower Li-ion capacities than those with small particle sizes³¹. These Co particles have slightly larger particle sizes and higher crystallinity compared with those of metal nanoparticles produced by the electrochemically driven conversion reaction (~ 2 nm)^{22,32}, which explains why our chemically synthesized N-Co/N- Li_2O composite has a higher OCV and charge potential than that obtained from the electrochemically driven conversion reaction. In contrast, with much bigger Co particles and looser contact between Co and Li_2O , the M-Co/N- Li_2O composite and SM-Co/N- Li_2O composites exhibit a higher charge potential and deliver a very low specific charge capacity in the same applied potential range (Fig. 2b and Supplementary Fig. 16).

To understand the Li-extraction process from the N-Co/N- Li_2O composite, we carried out an *in situ* TEM electrochemical measurement. The set-up of the *in situ* TEM electrochemical device is based on previous studies^{33,34}. As shown in Fig. 3d,e, our electrochemical micro-cell consists of the N-Co/N- Li_2O composite as the working electrode and a template-fabricated hollow carbon fibre³⁵ as the counter electrode. The Li_2O layer on the surface of the working electrode also acts as a solid electrolyte. A voltage bias is applied to drive the reverse conversion reaction and extract Li from the working electrode towards the carbon counter electrode. A series of TEM images for a N-Co/N- Li_2O particle aggregate are recorded during the delithiation process (Fig. 3f and Supplementary Video 1). The results show that, immediately after application of the voltage bias, the initial particles start to shrink, indicating that the Li is being extracted. Taking into account the initial size of the N-Co/N- Li_2O particle aggregate, less than half of its initial volume is retained after the delithiation. Furthermore, the fact that the Li transfers from the N-Co/N- Li_2O working electrode to the carbon counter electrode is effectively confirmed by the EELS spectra taken on the carbon counter electrode before and after the delithiation process (Fig. 3g). On Li extraction, Co may undergo multiple oxidation states, such as CoO, Co_3O_4 and some other possible transition states. The intermediate CoO at the half-charge state was confirmed by the XPS investigation (Supplementary Fig. 17). Multiple intermediate phases and oxidation states of Co may lead

to the multi-step voltage trend on the Li-extraction process from the Co/ Li_2O nanocomposite (Fig. 2b). The product obtained after delithiation is confirmed as Co_3O_4 by XPS, indicating its reverse conversion-reaction mechanism: $3\text{Co} + 4\text{Li}_2\text{O} \rightarrow \text{Co}_3\text{O}_4 + 8\text{Li}$ (Supplementary Fig. 17).

Generalization to other metal/ Li_2O nanocomposites

To show the generality of using N-M/N- Li_2O composites as high-capacity cathode additives, we also prepared N-Ni/N- Li_2O and N-Fe/N- Li_2O composites using the same synthesis procedure. Their composition of M and Li_2O is confirmed by the XRD results (Supplementary Fig. 18). Working electrodes were prepared for N-Ni/N- Li_2O and N-Fe/N- Li_2O composites, respectively. As shown in Fig. 4a,b, the N-Ni/N- Li_2O and N-Fe/N- Li_2O electrodes exhibit different potential profiles on the first-cycle charge process, probably owing to the difference between the M atoms and particle size. Similar to the N-Co/N- Li_2O composite, they possess a high initial OCV (higher than 1.5 V) and deliver high charge capacities of 506 and 631 mAh g^{-1} , respectively, and very low discharge capacities of 11 and 19 mAh g^{-1} , respectively (Fig. 4a,b). The LiFePO_4 electrodes with the two additives were both subject to cycling (Fig. 4c,d). As expected, their first-cycle charge capacities are improved significantly. The initial charge capacities are 180 mAh g^{-1} for the electrode with a 4.8% N-Ni/N- Li_2O additive and 178 mAh g^{-1} for that with a 4.8% N-Fe/N- Li_2O composites. These capacities are $\sim 10\%$ higher than those of LiFePO_4 electrodes without any prelithiation additive. Moreover, these electrodes also show very good cycling stability (Fig. 4e,f).

Conclusions

In summary, we propose a design principle for cathode prelithiation to compensate the first-cycle Li loss in Li-ion batteries. Experimentally, we demonstrate a class of nanoscale mixtures of M and Li_2O which exhibit high prelithiation efficacy by exploiting the unique characteristics of high specific capacity and large potential hysteresis of the conversion reaction. With such a cathode prelithiation additive, the specific capacity and energy density of a LiFePO_4 /graphite full cell are appreciably improved. The as-made nanocomposites are promising high-capacity prelithiation materials that are potentially compatible with existing industrial battery fabrication processes. Owing to their superior performance as a Li donor, we believe that these conversion-reaction-based cathode additives will have important applications in existing Li-ion batteries, as well as future advanced battery systems involving high-capacity anodes (for example, Si and Sn) with large first-cycle capacity loss.

Methods

Materials synthesis. To synthesize the N-Co/N- Li_2O composite, Co_3O_4 nanoparticles (2 mmol, 99.5%, Sigma-Aldrich) were reacted with molten Li metal (16 mmol, 99.9%, Alfa Aesar) at 185 °C for 20 min and 200 °C for 2 h under continuous mechanical stirring in an argon-filled glove box with a moisture level below 0.1 ppm and oxygen level below 3.0 ppm. To eliminate the residual Li metal, the synthesized composite was stored in dry air before use. N-Ni/N- Li_2O and N-Fe/N- Li_2O composites were prepared using the same procedure with NiO (8 mmol, 99.8%, Sigma-Aldrich) and Fe_3O_4 (2 mmol, 97%, Sigma-Aldrich) nanoparticles as the starting materials. The molar ratios of MOs and Li were designed according to their reaction ($\text{M}_x\text{O}_y + 2y\text{Li} \rightarrow x\text{M} + y\text{Li}_2\text{O}$). Li_2O nanoparticles and micrometre-sized cobalt particles were obtained by subjecting commercial Li_2O particles (97%, Sigma-Aldrich) and Co particles (99.8%, Sigma-Aldrich) to a mechanical milling technique, separately. The as-obtained Li_2O nanoparticles and micrometre-sized Co particles were mixed uniformly according to a molar ratio of 4:3 to achieve the M-Co/N- Li_2O composite. After further mechanical milling of the M-Co/N- Li_2O composite, the SM-Co/N- Li_2O composite was prepared.

Characterization. The XRD measurements were performed using a Panalytical X'pert diffractometer with Ni-filtered Cu K α radiation ($\lambda = 1.5406$ Å). XPS analyses were conducted with a PHI Versa Probe 5000 system (Physical

Electronics). A FEI Titan 80–300 environmental TEM was employed for HRTEM and STEM images, EDS and EELS mapping collection, and *in situ* TEM measurements. A Nanofactory Instruments Dual-Probe STM-TEM *in situ* sample holder was employed to demonstrate the delithiation process for the N-Co/N-Li₂O composite. During the measurement, a relative bias of 6 V was applied between the N-Co/N-Li₂O working electrode and the hollow carbon fibre counter electrode, which caused the inverse conversion reaction to extract Li from the working electrode and transfer it to the counter electrode. EELS spectra were taken on the carbon electrode before and after delithiation of the N-Co/N-Li₂O composite.

Electrochemical measurements. The battery performance was assessed using a 2032-type coin cell (MTI Corporation) on an Arbin Battery Cycler instrument. The cells were assembled in an argon-filled glove box using 1 M LiPF₆ in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 v/v) as the electrolyte and a Celgard 2300 membrane as the separator. The slurry coating for electrode fabrication was carried out at ambient conditions by mixing the active materials, carbon black and polyvinylidene fluoride (PVDF) binder in *N*-methyl-2-pyrrolidone (NMP) solvent. The electrodes were then dried in vacuum at 60 °C. The M/Li₂O electrodes consisted of 60% M/Li₂O composite, 30% carbon black and 10% PVDF binder in weight, with a typical loading of ~1 mg cm⁻². Commercial LiFePO₄ powder (MTI Corporation) and the as-synthesized cathode additives were mixed at different weight ratios as the active hybrid cathode materials. LiFePO₄ electrodes were prepared with 80% of these hybrid cathode materials, 10% carbon black and 10% PVDF. Their typical mass loading is ~5 mg cm⁻². Graphite electrodes were made by mixing the graphite powder (MTI Corporation), carbon black and PVDF with a mass ratio of 8:1:1. The active loading of the anode was 2.3 mg cm⁻². The capacity ratio of the negative electrode to the positive electrode (N/P ratio) used for the full-cell test was 1.02. M/Li₂O/Li metal half cells were charged to 4.1/4.3 V and discharged to 2.5 V at a current density of 50 mA g⁻¹. The galvanostatic charge/discharge measurement for LiFePO₄/Li metal half cells was carried out in the cutoff potential range 2.5–4.2 V. The cutoff potential range for LiFePO₄/graphite full cells is 1.5–4.2 V. The current density for LiFePO₄ electrodes is 0.1 C for the first cycle and 0.2 C for the following cycles.

Received 15 June 2015; accepted 12 November 2015;
published 11 January 2016

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Acknowledgements

Y.C. acknowledges the support from the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the US Department of Energy under the Battery Materials Research (BMR) Program. S. Lee and G. Zheng are acknowledged for discussions and help.

Author contributions

Y.S. and Y.C. conceived and designed the experiments. Y.S. performed materials fabrication, characterization and electrochemical measurements. H.-W.L. conducted *in situ* TEM and HR-TEM characterization. Y.S. and Y.C. co-wrote the paper. All authors discussed the results and commented on the manuscript.

Additional information

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Competing interests

The authors declare no competing financial interests.