Conformal Prelithiation Nanoshell on LiCoO$_2$

Enabling High Energy Lithium-Ion Batteries

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ABSTRACT

Lithium-ion batteries (LIBs) using LiCoO$_2$ cathode and graphite anode are dominating portable devices. However, their energy density is reaching the theoretical limit. Using high-capacity Si-based materials to replace graphite can increase the energy density of LIBs and meet the increased demand for various applications. Nevertheless, the low initial Coulombic efficiency of Si-based anode consumes large amounts of electrochemically active lithium (15% or higher) from the cathode and reduces the energy density of LIBs. Herein, we report in-situ formation of conformal ultrathin lithium-rich nanoshell (Li$_2$O/Co, ~20 nm) on LiCoO$_2$ particles as a high-capacity built-in prelithiation reagent using a simple and scalable chemical solution route. During the initial charge process, this nanoshell undergoes irreversible reactions ($4\text{Li}_2\text{O} + 3\text{Co} \rightarrow 8\text{Li}^+ + 8\text{e}^- + \text{Co}_3\text{O}_4$, $2\text{Li}_2\text{O} \rightarrow 4\text{Li}^+ + 4\text{e}^- + \text{O}_2\uparrow$) and delivers high lithium-ion capacity (903 mAh g$^{-1}$ in theory based on the Li$_2$O/Co ratio of 2/1), which can compensate the initial lithium loss at the Si-based anode and improve the energy density of LIBs. Importantly, such core-shell structured LiCoO$_2$ (CS-LiCoO$_2$) is compatible with the current battery fabrication process. Experimentally, we show a 10% increase (15 mAh g$^{-1}$) in overall charge capacity for the CS-LiCoO$_2$ with 1.5 wt% of Li$_2$O/Co in comparison to the pristine LiCoO$_2$ during the initial charge process. Paired with graphite-SiO anode, a full cell using CS-LiCoO$_2$ cathode demonstrates 11% higher discharge capacity (2.60 mAh cm$^{-2}$) than that using pristine LiCoO$_2$ (2.34 mAh cm$^{-2}$) at 0.1 C. Also, 81% capacity retention was achieved for the CS-LiCoO$_2$$\parallel$graphite-SiO cell at 0.2 C after 100 cycles. The simple and scalable synthesis, compatibility with the current battery industry, and the effect in improving the energy density of full batteries make the CS-LiCoO$_2$ material promising for large-scale commercialization.

KEYWORDS: lithium-ion batteries, cathode prelithiation, LiCoO$_2$, high energy
Lithium-ion batteries (LIBs) using LiCoO$_2$ as the cathode and graphite as the anode are the dominant power sources for portable electronics.$^{1-3}$ Since their commercialization by Sony in 1991, the energy density of LiCoO$_2$||graphite batteries has been increasing from 75 to over 200 Wh kg$^{-1}$ accompanied by the improvement of electrode materials and electrolytes, which is approaching the limit with regard to the theoretical capacity of graphite (372 mAh g$^{-1}$), practical reversible capacity of LiCoO$_2$ ($\sim$140 mAh g$^{-1}$) and electrochemical window of current electrolytes (< 4.3 V). The further increase in energy density of the LiCoO$_2$-based LIBs relies on the development of stabilized LiCoO$_2$ that can release higher reversible capacity (e.g., > 160 mAh g$^{-1}$) in a wider working potential window (e.g., 3–4.5 V),$^{4-6}$ electrolytes with larger electrochemical window (e.g., 0–4.5 V)$^{7-9}$ and Si-based anode with higher capacity (e.g., > 450 mAh g$^{-1}$) in comparison to those in traditional commercial LIBs.$^{10,11}$ Si-based anode ranks among the most promising alternatives for the current commercial pure graphite anode for next-generation high-energy density LIBs due to its higher capacity and similar working potential.$^{12}$ However, Si-based anode suffers from much lower initial Coulombic efficiency than graphite, typically ~85% for the graphite-Si or graphite-SiO composite with a capacity of ~ 450 mAh g$^{-1}$, which further decreases with increased Si content. In other words, appreciable amount of active lithium from cathode is consumed accompanied by the formation of a solid electrolyte interphase (SEI) on the anode surface during the initial battery charging process. This initial lithium loss significantly reduces the overall capacity and energy density of LIBs.

LiCoO$_2$ cathode is the only lithium source in LIBs with a lithium-free graphite or Si-based anode. Loading additional LiCoO$_2$ at the cathode side can compensate this initial lithium loss. However, this approach would increase the mass loading at the cathode side and the improvement in energy density is very limited due to the low practical lithium-ion capacity of LiCoO$_2$ (~140
mAh g$^{-1}$). Electrochemical prelithiation approaches (e.g., discharging a Si nanowire||Li metal cell) showed high lithium compensation efficiency, but the complex operation limits their practical application.$^{13,14}$ Prelithiation additives are promising to compensate the initial lithium loss. Stabilized lithium metal powders (SLMP), lithium silicide, and Li$_2$Z-Li$_2$O composites (Z = Si, Ge, Sn, etc.) can be effective lithium donors to offset the initial lithium loss when used as anode prelithiation additives and introduced into the anode due to their high lithium-ion capacities.$^{15-18}$ However, their high chemical reactivity makes them challenging for practical application, which causes safety concerns and is not compatible with the regular industrial slurry-based electrode fabrication using N-methyl-pyrrolidone (NMP) or water as the solvent. Although cathode prelithiation additives, such as Li$_2$NiO$_2$, Li$_6$CoO$_4$ and Li$_5$FeO$_4$, show better stability than anode prelithiation additives, their “donor” lithium-ion capacity is limited (e.g., < 400 mAh g$^{-1}$).$^{19-21}$ Li$_2$O, Li$_2$O$_2$ and Li$_3$N can release high “donor” lithium-ion capacity, but their application as prelithiation additives is not compatible with current battery or electrode manufacturing process.$^{22-24}$ Recently, we successfully fabricated a series of cathode prelithiation additives (Li$_2$O/M, M = Fe, Co and Ni, etc) through the reaction between metal oxide and molten lithium, which released high “donor” lithium-ion capacities (e.g., > 600 mAh g$^{-1}$) based on inverse conversion reaction (Li$_2$O/M → M + xLi$^+$ + xe$^-$) in the initial battery charge process and improved the reversible capacity and energy density of the full cells up to 11%.$^{25-27}$ However, facile materials synthesis with high safety should be explored before their scale up application.

Prelithiation materials for LIBs should follow the guidelines below in consideration of the practical application: (1) High “donor” lithium-ion capacity during the initial charging process without causing negative effects on cycle life or rate capability of the LIBs. (2) Controllable prelithiation degree, which is critical for the capacity matching between the cathode and anode to
maximize the overall energy density of LIBs. (3) Good compatibility with the current battery fabrication processes, including slurry fabrication, electrode drying, and battery assembly. (4) Simple and straightforward materials processing with low cost and high safety.

Herein, we propose the rational design of functional cathode that consists of active material with high-capacity built-in prelithiation reagent in each single particle. The built-in prelithiation reagent can provide high “donor” lithium-ion capacity during the first cycle to compensate the initial lithium loss, and the active material can release reversible capacity for battery cycling. Experimentally, a simple and low cost solution chemistry route utilizing the reaction between LiCoO$_2$ and a lithium complex (lithium naphthaline, Naph-Li, Li$^{+}$C$_{10}$H$_{8}^-$) solution was used to in-situ generate a conformal ultrathin Li$_2$O/Co nanoshell on LiCoO$_2$ particles. It is noteworthy that the reaction between LiCoO$_2$ and lithium complex is controllable. The thickness of the Li$_2$O/Co nanoshell can be tuned to meet different requirement of lithium compensation for batteries using different anodes. Importantly, the materials, electrode and battery processing can be carried out using current industrial technology for the as-achieved CS-LiCoO$_2$. In comparison to using independent prelithiation materials, our implanted prelithiation reagent in cathode materials simplifies the electrode fabrication process and enables more uniform prelithiation in comparison to using individual prelithiation reagents. Therefore, our strategy for the compensation of the initial lithium loss and increase of energy density of LIBs meets the as-mentioned criteria for scalable application. As an example, we showed that the CS-LiCoO$_2$ with appropriate prelithiation (1.5 wt% Li$_2$O/Co in the CS-LiCoO$_2$) exhibited 15 mAh g$^{-1}$ higher charge specific capacity than the pristine LiCoO$_2$ (165 mAh g$^{-1}$ for the CS-LiCoO$_2$ vs. 150 mAh g$^{-1}$ for the pristine LiCoO$_2$) at 0.1 C. A CS-LiCoO$_2$||graphite-SiO full cell exhibited higher capacity and energy density than the
counterpart using pristine LiCoO$_2$ as well (533 Wh kg$^{-1}$ for CS-LiCoO$_2$||graphite-SiO cell vs. 481 Wh kg$^{-1}$ for LiCoO$_2$||graphite-SiO cell).

**Results and discussions.** LiCoO$_2$ is a well-known conventional layered cathode in the typical R$ar{3}$m space group with the $a$-NaFeO$_2$ crystal structure (Figure S1). Lithium ions are occupied between the octahedral metal oxide slabs within the structure, and can be reversibly extracted/inserted through the topotactic reaction.$^{28}$ When additional lithium ions are electrochemically introduced into LiCoO$_2$, continuous electrochemical conversion takes place to form a Li$_2$O/Co nanocomposite (LiCoO$_2$ + $3$Li$^+$ + $3$e$^-$ $\rightarrow$ $2$Li$_2$O + Co, Figure 1a).$^{29,30}$ This reaction starts from the surface of LiCoO$_2$ particles and gradually penetrates the entire particle. Before the full lithiation, LiCoO$_2$ and Li$_2$O/Co coexist as the intermediates, with tiny amount of Li$_2$O/CoO at their interface.$^{31}$ These results make it possible to fabricate Li$_2$O/Co or Li$_2$O/CoO/Co nanocomposite on each single LiCoO$_2$ particle as a built-in high-capacity prelithiation material via an electrochemical and/or chemical route. While the reaction for the fabrication of Li$_2$O/Co nanocomposite on LiCoO$_2$ particles is precisely controllable using electrochemical process by assembling electrochemical cell, it is time consuming and the operation is complex and not suitable for the practical industrial application. Here, a simple and controllable solution based reaction was explored to *in-situ* form a Li$_2$O/Co nanocomposite shell on LiCoO$_2$ utilizing the chemical reaction between lithium complex (Li$^+$B$^-$) and LiCoO$_2$ at room temperature (Figure 1b). Li$^+$B$^-$ is composed of a positively charged lithium ion (Li$^+$) and a negatively charged organic ligand (B$^-$).$^{32}$ Lithium naphthalene (Naph-Li, Li$^+$C$_{10}$H$_8^-$) complex was chosen in virtue of its low cost and easy preparation. During the synthesis, 0.2 M Naph-Li solution in tetrahydrofuran (THF) was prepared through the reaction between metallic Li and naphthalene in THF at room temperature. The LiCoO$_2$ powder was then immersed into the as-fabricated Naph-Li solution. Electrons transferred
from C_{10}H_8^- to the surface of LiCoO_2 particles, and Li^+ ions incorporated into LiCoO_2 simultaneously during the reaction, leaving uncharged state naphthalene in the THF solution. Residual naphthalene in the LiCoO_2 cathode could be easily removed during the washing and baking process due to its high solubility in THF and low sublimation temperature (Figure S2). By controlling the ratio of Naph-Li and LiCoO_2 (molar ratio of 3.7/100), 1.2 wt% of the LiCoO_2 was chemically lithiated, corresponding to 1.5 wt% of Li_2O/Co in the CS-LiCoO_2. The reaction solution turned from the initial dark blue to light yellow after 3 minutes, indicating the fast reaction between Naph-Li and LiCoO_2 (Figure S3). Finally, a Li_2O/Co nanoshell was in-situ formed uniformly on the very surface of LiCoO_2 particles. Note that the remaining naphthalene in the THF solution can be reused to fabricate the Naph-Li solution, making the fabrication of CS-LiCoO_2 recyclable and low-cost. Only active lithium was introduced into the LiCoO_2 cathode through such a facile processing and thus high prelithiation efficiency for the as-achieved prelithiation material (Li_2O/Co) could be expected. We can tune the content of Li_2O/Co composite in the CS-LiCoO_2 through regulating the initial amount of LiCoO_2 and Li-Naph (Figure S4). The simple solution-based chemical prelithiation route avoids the complicated operation process for electrochemical prelithiation and is more efficient in comparison to the synthesis and use of individual cathode prelithiation reagents, making it a promising strategy for addressing the initial lithium loss in LIBs.

The morphology and structure of the CS-LiCoO_2 were investigated using scanning electron microscopy (SEM), X-ray diffraction (XRD) and transmission electron microscopy (TEM). Figure S5a and b compared the SEM images of the pristine LiCoO_2 and CS-LiCoO_2. They both consisted of micrometer-sized irregular particles with similar morphology. No cracks or breaking was observed for the CS-LiCoO_2 particles, indicating the chemical prelithiation only took place on the very surface layer of LiCoO_2 particles, but did not penetrate single LiCoO_2 particles and cause
collapse due to the chemical conversion reaction with large volume expansion. In addition, there was no change in XRD peaks for CS-LiCoO₂ in comparison to the pristine LiCoO₂ (Figure 1c), suggesting that only very small amount of LiCoO₂ converted to Li₂O/Co during the chemical conversion reaction. The composition and electronic structure of the surface layer of the CS-LiCoO₂ were investigated by X-ray photoelectron spectroscopy (XPS). High-resolution Co 2p, Co 3p and Li 1s spectra for the pristine LiCoO₂ and CS-LiCoO₂ were compared in Figure 1d and e.

In comparison with the pristine LiCoO₂, the peaks for Co 2p and Co 3p of CS-LiCoO₂ broadened and shifted to lower binding energy, demonstrating that Co element on the surface of CS-LiCoO₂ was reduced during the chemical prelithiation process. Signals for Co metal (793.6 eV and 778.1 eV for Co⁰ 2p₁/₂ and Co⁰ 2p₃/₂, respectively) were observed in the Co 2p spectra (Figure 1d), indicating the formation of Co nanoparticles during the chemical prelithiation reaction. Moreover, the CS-LiCoO₂ exhibited much stronger peak for Li 1s in comparison to the pristine LiCoO₂, demonstrating the successful formation of a lithium rich layer on LiCoO₂ particles during the chemical prelithiation reaction. Smooth surface was observed for a pristine LiCoO₂ particle under TEM and its nature of the single crystal is revealed by high-resolution TEM (HRTEM) image that shows the clear interplanar spacing of 0.24 nm corresponding to the (101) plane of LiCoO₂. After chemical prelithiation, a thin layer of ~20 nm was formed on the surface of LiCoO₂ particles (Figure 1f and S5c). The HRTEM image of the Li₂O/Co composite was shown in Figure 1g. Abundant crystalline nanoparticles with diameter of less than 5 nm was observed. These crystalline nanoparticles showed interplanar spacings of 0.19 nm and 0.21 nm corresponding to (101) and (100) plane for metallic Co, respectively. Electron energy loss spectroscopy (EELS) was further conducted for the surface layer of the CS-LiCoO₂ (Figure 1h). It is confirmed that the Li in LiCoO₂ was transformed to Li₂O after prelithiation. As such, an
ultrathin surface layer of Li$_2$O/Co nanocomposite with thickness of ~20 nm was successfully formed on LiCoO$_2$ particles to produce CS-LiCoO$_2$ through the chemical reaction between LiCoO$_2$ and Naph-Li solution, which was consistent with the XPS results. This ultrathin Li$_2$O/Co nanolayer can be employed as built-in prelithiation reagent of LiCoO$_2$ to provide high lithium-ion capacity and compensate the lithium loss at the anode and contribute to the improvement of the energy density of LIBs. Moreover, the result observed here regarding the structural change of LiCoO$_2$ during lithiation is also well consistent with the electrochemical prelithiation of LiCoO$_2$ or its chemical lithiation observed using in situ TEM measurement.$^{31}$

The electrochemical performance of the pristine LiCoO$_2$ and CS-LiCoO$_2$ was investigated by galvanostatic charge-discharge measurement in the potential range of 3−4.2 V in half cells using lithium metal as the counter electrode at 0.1 C (1 C = 140 mAh g$^{-1}$). Figure 2a and b showed the initial charge-discharge curves for the pristine LiCoO$_2$ and CS-LiCoO$_2$ electrodes. Overall, both electrodes exhibited similar voltage curves. It was noted that several small voltage plateaus were observed during the initial charge process below 3 V for the CS-LiCoO$_2$ electrode, which were different from the pristine LiCoO$_2$ electrode. Correspondingly, the differential capacity versus voltage (dQ/dV) profiles of the CS-LiCoO$_2$ electrodes (Figure S6) displayed obvious peaks in this voltage range. We further analyzed the cyclic voltammograms (CVs) for the pristine LiCoO$_2$ and CS-LiCoO$_2$ electrodes (Figure 2c). Several new oxidation peaks appeared between 1.7 to 2.7 V in the CVs of the CS-LiCoO$_2$ electrode in comparison to the pristine LiCoO$_2$ at a scan rate of 0.1 mV s$^{-1}$, well consistent with their charge-discharge profiles (Figure 2a and b). These new voltage plateaus or oxidation peaks for the CS-LiCoO$_2$ can be ascribed to the electrochemical lithium extraction from the Li$_2$O/Co nanocomposite, which can enable increased initial charge specific capacity for the CS-LiCoO$_2$ in comparison to the pristine LiCoO$_2$. The increased capacity during
this voltage range was 8 mAh g\(^{-1}\), which was close to the theoretical capacity contribution based on the inverse conversion reaction (4Li\(_2\)O + 3Co \(\rightarrow\) 8Li\(^+\) + 8e\(^-\) + Co\(_3\)O\(_4\)). The slopes/plateaus between 3.7 to 4.2 V for both electrodes arose from the reversible extraction and insertion of lithium ions from/into the structure of LiCoO\(_2\), contributing to the reversible capacity of LiCoO\(_2\). Interestingly, the capacity during this voltage range for the CS-LiCoO\(_2\) was \(~7\) mAh g\(^{-1}\) higher than pristine LiCoO\(_2\) electrode. This increased capacity should be mainly contributed by the decomposition of residual Li\(_2\)O in the nanoshell (2Li\(_2\)O \(\rightarrow\) 4Li\(^+\) + 4e\(^-\) + O\(_2\)↑).\(^{22}\) As expected, due to the capacity contribution from the prelithiation nanolayer of Li\(_2\)O/Co, the overall voltage-capacity curve of the CS-LiCoO\(_2\) electrode shifted right and a high initial charge capacity of 165 mAh g\(^{-1}\) was delivered, which was 15 mAh g\(^{-1}\) higher than that for the pristine LiCoO\(_2\) (150 mAh g\(^{-1}\)). The initial discharge curves of the pristine LiCoO\(_2\) and CS-LiCoO\(_2\) overlapped well and their discharge capacities were 145 and 150 mAh g\(^{-1}\), respectively, suggesting no negative effect on the discharge process of LiCoO\(_2\) for the chemical prelithiation treatment of LiCoO\(_2\). The slightly increased discharge capacity of the CS-LiCoO\(_2\) may come from the activation of LiCoO\(_2\) during the materials processing. XRD was further conducted to investigate the structure information of the pristine LiCoO\(_2\) and CS-LiCoO\(_2\) at the discharge (to 3 V) and charge (to 4.2 V) states (Figure S7). The pristine LiCoO\(_2\) and CS-LiCoO\(_2\) exhibited similar evolution for the locations and intensities of XRD peaks and no additional peaks were detected for the CS-LiCoO\(_2\), suggesting that the chemical prelithiation did not cause the change in the reversible electrochemical lithium storage mechanism for LiCoO\(_2\). Information for the structure and composition of the CS-LiCoO\(_2\) after a full charge and discharge cycle was also investigated using TEM and XPS. Observed under TEM, the thickness of the initial surficial layer on CS-LiCoO\(_2\) was slightly reduced and maintained close contact with the LiCoO\(_2\) core (Figure S8). Co\(_3\)O\(_4\) nanocrystals with an average particle size
of ~5 nm were observed on the surface of the CS-LiCoO₂ after 1 charge/discharge cycle (Figure 2d), demonstrating the oxidation of metallic Co and the irreversible extraction of lithium from the Li₂O/Co composite nanolayer in the working voltage range of LiCoO₂. The peak location of Co 2p in the high-resolution Co 2p XPS spectra shifted to higher binding energy (798.2 and 782.8 eV for Co²⁺, and 796.2 and 780.6 eV for Co³⁺) after 1 charge/discharge cycle (Figure 2e), indicating the conversion of the initial Co state (metal Co) to a higher oxidation state (Co₃O₄).³³,³⁵ The peak intensity of Li 1s was significantly reduced, which elucidated that lithium in the surficial layer of the CS-LiCoO₂ was irreversibly extracted during the charging process. These results revealed that the Li₂O/Co nanocomposite transferred to Co₃O₄ and thus could deliver high lithium-ion capacity during the charging process of the CS-LiCoO₂, and would not be lithiated in the discharging process (Figure 2f). The conversion reaction of cobalt oxides takes place below 2 V, which is far below the cut-off voltage of LiCoO₂ (e.g., 3 V or even higher). As such, the as-produced Co₃O₄ would not be lithiated anymore after the first cycle during cycling. The “donor” lithium ions in the first-cycle charge process can compensate the initial lithium loss at the anode side, allowing more electrochemically active lithium to be available and improving the energy density of LIBs. Since the extraction of lithium from Li₂O/Co only takes place during the 1st charge process, it will not have any negative effect on the following cycling. After donating lithium in the first charging process, the generated thin Co₃O₄ shell on CS-LiCoO₂ cathode would remain unchanged during the following cycles. According to the above discussion, therefore, the Li₂O/Co nanoshell of CS-LiCoO₂ is promising as built-in prelithiation material, which can compensate the lithium loss at the anode side and enable increased energy density for LIBs.

Figure 3a showed the charge/discharge curves of the CS-LiCoO₂ electrode in lithium metal half cell after the first cycle at 1 C. The oxidation peaks below 3 V in the first-cycle charging process
(Figure 2a) disappeared and the LiCoO$_2$ and CS-LiCoO$_2$ electrodes showed similar voltage-capacity plots in the following cycles (Figure 3a and Figure S9), suggesting the electrochemical lithium extraction process from the Li$_2$O/Co nanocomposite only took place in the first cycle. Moreover, the pristine LiCoO$_2$ and CS-LiCoO$_2$ electrodes displayed similar electrochemical cycling stability (Figure 3b) and structure stability for 100 cycles (Figure S10), demonstrating that the chemical prelithiation here did not cause any negative effects on LiCoO$_2$. Besides, both electrodes maintained their initial structure (Figure S11) and showed similar EIS results on cycling (Figure S12), again verifying that the chemical prelithiation posed no threat to the cycling performance of the LiCoO$_2$ cathode.

With high “donor” lithium-ion capacity in the first cycle, the CS-LiCoO$_2$ electrode is promising for pairing with high-capacity graphite-SiO anode to compensate the initial lithium loss and produce LIBs with high energy density. Since Li$_2$O/Co nanocomposite is in-situ formed on the surface of CS-LiCoO$_2$ and works as a built-in prelithiation reagent, no additional additive needs to be involved as an individual component during the slurry and electrode fabrication, which makes the processing industrially feasible. At a high mass loading of active material in cathodes (~18.5 mg cm$^{-2}$), the CS-LiCoO$_2$||graphite-SiO cell delivered higher discharge capacities than the LiCoO$_2$||graphite-SiO cell in the initial cycle at 0.1 C (141 mAh g$^{-1}$ and 2.60 mAh cm$^{-2}$ for CS-LiCoO$_2$||graphite-SiO vs. 127 mAh g$^{-1}$ and 2.34 mAh cm$^{-2}$ for LiCoO$_2$||graphite-SiO, Figure 3c). Note that this specific capacity here was based on the total mass of LiCoO$_2$ or CS-LiCoO$_2$. This result indicated that the initial lithium loss at the graphite-SiO anode was successfully compensated by the “donor” lithium ions from the Li$_2$O/Co composite and thus the overall energy density of batteries was significantly increased. The energy density of the CS-LiCoO$_2$||graphite-SiO cell was 533 Wh kg$^{-1}$, which was much higher than 481 Wh kg$^{-1}$ for the pristine LiCoO$_2$||graphite-SiO cell,
which was calculated based on the total mass of the cathode material. The charge-discharge curves and cycling stability were further compared for the CS-LiCoO$_2$∥graphite-SiO and pristine LiCoO$_2$∥graphite-SiO cells (Figure S13 and Figure 3d). After 100 cycles at a current density of 0.2 C, the CS-LiCoO$_2$∥graphite-SiO cell still delivered a specific capacity of 112 mAh g$^{-1}$ and an areal capacity of 2.09 mAh cm$^{-2}$, much higher than of 90 mAh g$^{-1}$ and 1.65 mAh cm$^{-2}$ for the pristine LiCoO$_2$∥graphite-SiO cell.

The ambient stability of the as-fabricated material is important in consideration of its practical application in battery industry. The electrochemical performance of CS-LiCoO$_2$ electrodes were evaluated after exposure to ambient air condition for different time (3, 6 and 12 h). As shown in Figure 4a and b, the charge voltage plateaus of CS-LiCoO$_2$ electrode in the potential range of 1.7-2.7 V became weaker with the increase of exposure time in air. After 12 hours’ exposure to ambient air, the increased charge capacity of the CS-LiCoO$_2$ was 7 mAh g$^{-1}$ in comparison to the pristine LiCoO$_2$ (Figure 4c), which was about half of the initial increased capacity (15 mAh g$^{-1}$). Note that 12 hours is long enough for the electrode processing and better capacity retention can be achieved in dry room that is widely used in battery industry. Correspondingly, the discharge capacity slightly decreased with the increase of exposure time in ambient air. The discharge capacity of the CS-LiCoO$_2$ electrode after 12 hours’ exposure was close to that of the pristine LiCoO$_2$ (~ 145 mAh g$^{-1}$). Good cycling stability was achieved for all the tested electrode (Figure 4d), which suggested that the exposure to ambient condition did not affect the cycling stability of the active LiCoO$_2$ in the CS-LiCoO$_2$. The decrease of the charge capacity is attributed to the side reactions of Li$_2$O with moisture in the air.

**Conclusion.** In summary, we developed a facile and efficient solution chemistry route to form a built-in prelithiation material on the surface of LiCoO$_2$ to offset the initial lithium loss at the anode
and improve the energy density of LIBs. Experimentally, we utilized the chemical reaction between Naph-Li solution and LiCoO$_2$, and enabled the conversion of surficial LiCoO$_2$ into Li$_2$O/Co composite nanolayer on LiCoO$_2$ and formed CS-LiCoO$_2$. Typically, a CS-LiCoO$_2$ electrode with 1.5 wt% Li$_2$O/Co showed 15 mAh g$^{-1}$ higher capacity than the pristine LiCoO$_2$ electrode during the first-cycle charging process. Moreover, high energy density of 533 Wh kg$^{-1}$ was achieved for the CS-LiCoO$_2$||graphite-SiO cell, which was 52 Wh kg$^{-1}$ higher than the cell using pristine LiCoO$_2$ electrode. Importantly, such a prelithiation process is facile, cost effective and recyclable. It is potentially compatible with the current industrial battery fabrication process as well. We believe that the proposed prelithiation technique will have important applications in the existing as well as next-generation LIB systems utilizing high-capacity Si-based anodes with large first-cycle irreversible lithium loss.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Experimental details; crystal structure of LiCoO$_2$; photographs of the reactants and reaction products; charge/discharge curves of the CS-LiCoO$_2$ electrodes with different degrees of prelithiation; SEM, TEM and dQ/dV profiles of the pristine LiCoO$_2$ and CS-LiCoO$_2$; XRD, TEM, SEM, and EIS characterizations of the cycled electrodes; voltage profiles of LiCoO$_2$||graphite/SiO and CS-LiCoO$_2$||graphite/SiO full cells

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Notes

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FIGURE CAPTIONS
Figure 1. (a) Capacity-voltage plot of LiCoO$_2$ during its electrochemical lithiation process at 0.1 C. Inset illustrates the intermediate products during the conversion reaction of LiCoO$_2$. (b) Schematic illustration of the preparation of CS-LiCoO$_2$. (c) XRD patterns and (d,e) high-resolution Co 2p, Co 3p, Li 1s XPS spectra of the pristine and CS-LiCoO$_2$. (f) TEM image of a CS-LiCoO$_2$ particle and (g) high-resolution TEM image on the edge of the CS-LiCoO$_2$ particle in f. (h) EELS spectra of the pristine LiCoO$_2$ and CS-LiCoO$_2$.

Figure 2. (a,b) The first-cycle charge/discharge curves of the pristine LiCoO$_2$ and CS-LiCoO$_2$ with interior box enlarged. (c) Magnification CV profiles of the pristine and CS-LiCoO$_2$ electrodes in the potential range of 1.5-2.9 V. (d) HR-TEM image and high-resolution (e) Co 2p, (f) Co 3p and Li 1s XPS spectra of the CS-LiCoO$_2$ cathode after the 1st charge/discharge process. Co$_3$O$_4$ nanocrystals were observed at the surface of the CS-LiCoO$_2$, indicating the irreversible lithium extraction from the initial Li$_2$O/Co composite. (g) Schematic illustration of the structure evolution of the CS-LiCoO$_2$ cathode during the 1st charge and the following charge/discharge cycles.

Figure 3. (a) Charge/discharge curves of CS-LiCoO$_2$ after the first cycle at 1 C. (b) Cycle comparison between pristine and chemical prelithiated CS-LiCoO$_2$ electrodes in half cells. (c) The first cycle charge/discharge curves and (d) cycling performance of the pristine LiCoO$_2$∥graphite/SiO and CS-LiCoO$_2$∥graphite/SiO full cells.

Figure 4. The first-cycle charge-discharge curves of the CS-LiCoO$_2$ electrodes exposed to ambient air condition for different time (3, 6, and 12 h). (b,c) The enlarged boxes of I and II in a. (d) Cycling performance of the CS-LiCoO$_2$ electrodes exposed to ambient air condition for different time (3, 6, and 12 h).
Figure 1
Figure 2
Figure 3