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ELECTROPLATING

Electroplating lithium transition metal oxides

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Materials synthesis often provides opportunities for innovation. We demonstrate a general low-temperature (260°C) molten salt electrodeposition approach to directly electroplate the important lithium-ion (Li-ion) battery cathode materials LiCoO₂, LiMn₂O₄, and Al-doped LiCoO₂. The crystallinities and electrochemical capacities of the electroplated oxides are comparable to those of the powders synthesized at much higher temperatures (700° to 1000°C). This new growth method significantly broadens the scope of battery form factors and functionalities, enabling a variety of highly desirable battery properties, including high energy, high power, and unprecedented electrode flexibility.

INTRODUCTION

Lithium transition metal oxides (LTMOs), which are typically synthesized in powder form via solid-state reactions at 700° to 1000°C, are nearly universally applied as cathode materials in Li-ion batteries. Because the current collector substrates used for Li-ion battery electrodes degrade at the LTMO synthesis temperatures (1), cathodes are made by slurry-casting the presynthesized LTMO powder onto either metal foils for conventional batteries or porous scaffolds (for example, fiber mats and open-cell foams) for emerging three-dimensional (3D) (2–4) and flexible battery designs (5, 6). However, the electrochemical and mechanical properties of slurry-cast electrodes are often limited by weak interconnections between particles and between the particles and the substrate (7, 8). We suggest that conformal electrodeposition of high-quality LTMOs would provide opportunities to enhance battery performance (energy density, power density, and flexibility) and broaden the scope of available electrode form factors (size, shape, porosity, and 3D integration). Whereas LTMOs are primarily used in batteries, LTMOs have also been considered for use as oxygen reduction catalysts (9) and anticorrosion layers (10), two applications where conformal deposition is important. Although atomic layer deposition (ALD) has been demonstrated to conformally grow LTMO films, as reviewed by Liu and Sun (11), the crystallinity and electrochemical performance of ALD-grown LTMOs is far inferior to those of conventionally synthesized LTMO powders. ALD is also not appropriate for thick films because of the very slow deposition rate. Before this report, electrodeposition, although successful for the syntheses of some oxide ceramics (12, 13), had not been demonstrated for the growth of high-quality LTMOs (14–20). Previously electroplated LTMOs exhibited poor electrochemical performance because of the inclusion of water, undesired cations,

transition metals at incorrect valance states, and disorder in the crystal structure (21, 22).

Here, we report a general low-temperature (~260°C) molten salt electrodeposition methodology to directly grow LTMOs (including layered LiCoO₂, spinel LiMn₂O₄, and Al-doped LiCoO₂), with crystallinities, and electrochemical performances, comparable to those made by traditional high-temperature (700° to 1000°C) routes. This method is compatible with a variety of conventional (for example, Al foil) and mesostructured current collectors, providing opportunities to realize new electrode architectures and functionalities. We demonstrate that a ~25-μm-thick, ~80% dense LiCoO₂ film can be directly electroplated on an Al foil, and the resultant full cell can deliver high-rate discharge up to at least 20 C. The high solubility of the transition metal salts in the molten hydroxide plating solution (see section SI), in conjunction with the plating solution's high ionic conductivity, minimizes the depletion of precursor ions during electrodeposition, allowing the formation of highly uniform deposits through mesostructured foams (see section SII) for ultrahigh areal capacities (for example, ~20 mA-hour cm⁻² for the 0.5-mm-thick LiCoO₂ electrode). When LTMOs are electroplated on a flexible network, such as a carbon nanofiber (CNF) paper (see figs. S1 and S2 and section SIII), intimate contact between the plated material and the current collector endows the electrode with superior flexibility, enabling fabrication of an ultraflexible battery using this cathode and a CNF-based anode that can cycle after being repeatedly bent 10,000 times from 0° to 180°.

RESULTS AND DISCUSSION

Electrodeposition of LiCoO₂ is carried out at 260°C in a near-eutectic mixture of LiOH, KOH, and CoO. To investigate the LiCoO₂ formation, cyclic voltammograms (CVs) of various working electrodes (CNF, Pt, Co, and Ni) are recorded using a Co wire as the quasi-reference electrode (see section SIV). In a CoO-free molten LiOH-KOH bath, gases are evolved at the CNF (Fig. 1A) and the Pt (Fig. 1B) working electrodes when the potential is greater than 1.2 V (slope S1) or below -0.25 V (slope S2), as the result of the oxidation (2OH⁻ → H₂O + 1/2O₂ + 2e) and reduction (2H₂O → 2OH⁻ + H₂ - 2e) of the hydroxide melt, respectively. Once CoO is added to the hydroxide melt (Fig. 1A), a hump at 1.0 V (P2) appears in the oxidation scan, corresponding to the formation of LiCoO₂ via electrooxidation of Co²⁺. In the reduction scan, Co²⁺ is reduced to Co metal below 0 V

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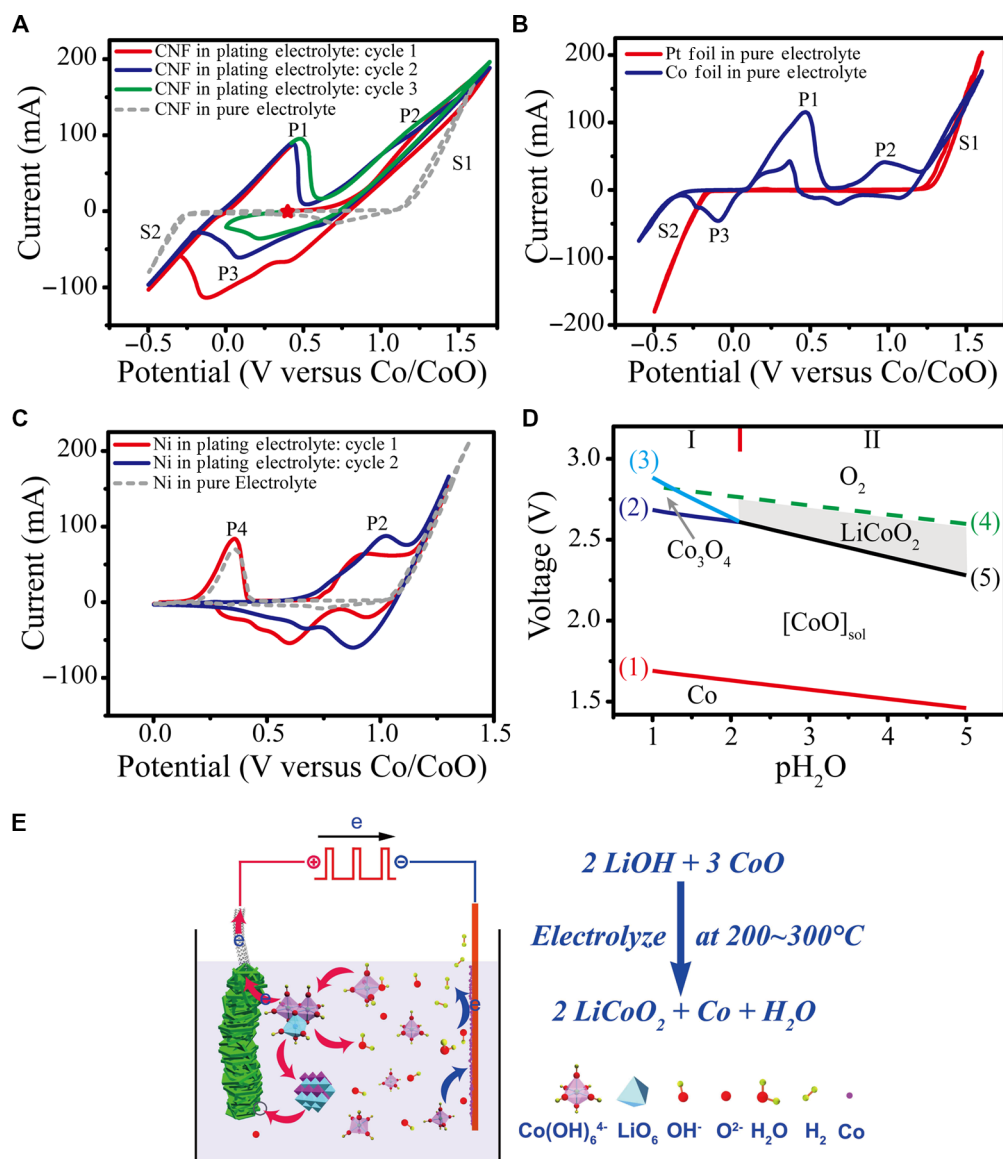


Fig. 1. Cyclic voltammetric and electrochemical modeling of KOH-LiOH-CoO eutectic systems. (A) CVs of CNF in pure and CoO-containing LiOH-KOH melts. (B) CVs of Co and Pt foils in pure LiOH-KOH melt. (C) CVs of Ni foil in pure and CoO-containing LiOH-KOH melts. (D) Potential- pH_2O diagram of the LiOH-KOH-CoO eutectic system. (E) Schematic illustration of electrodeposition process. All the CV measurements start from an oxidative scan.

(P3). When the working electrode is Co metal, Co is first oxidized to Co^{2+} around peak P1 (Fig. 1, A and B) and then transformed to LiCoO_2 at P2 (Fig. 1, A and B). Ni is oxidized at ~ 0.3 V (P4) in a pure hydroxide melt but exhibits no peak at 1.0 V (Fig. 1C). When CoO is added to the melt, LiCoO_2 starts to form on the Ni electrode at 1.0 V and appears to fully passivate the surface as peak P4 disappears after the first CV scan. On the basis of this analysis, we deduce that LiCoO_2 can be electrodeposited in a near-eutectic hydroxide melt at 260°C via the following reaction: $2\text{LiOH} + 3\text{CoO} \rightarrow 2\text{LiCoO}_2 + \text{Co} + \text{H}_2\text{O}$.

The LiCoO_2 formation mechanism is further evaluated by the thermodynamic potential- pH_2O diagram (Pourbaix diagram). In a hydroxide melt, H_2O acts as a Lux-Flood acid and accepts O^{2-} , turning into 2OH^- . The acidity, pH_2O [defined as $-\log(\chi_{\text{H}_2\text{O}})$, where $\chi_{\text{H}_2\text{O}}$ is the concentration of H_2O in the melt], plays an important role in determining the electroplating potential of each material and the thermodynamic stability of each compound. Figure 1D depicts two

electrochemical reaction regimes of greatest interest (see the modeling in section SV). Region I closely represents the conventional aqueous electrodeposition regime, in which Co_3O_4 is thermodynamically favorable because of the low formation potential (23, 24). As the melt becomes more basic, Co_3O_4 becomes unstable, and at the proper potential, pure LiCoO_2 forms. In region II (the shaded area), the oxygen line is at a higher voltage than the LiCoO_2 formation line, suggesting that oxygen gas can spontaneously oxidize CoO to LiCoO_2 , resulting in undesirable precipitation of LiCoO_2 in solution. LiCoO_2 electrodeposition is thus performed in an oxygen-free environment. The calculated phase diagram agrees well with the experimental CV result that it is possible to obtain LiCoO_2 in a hydroxide molten salt via an anodic electrochemical process, as shown in Fig. 1E.

Selective area electron diffraction is used to examine the electrodeposited LiCoO_2 and shows that the as-deposited material is O3- LiCoO_2 (O3 refers to the oxygen stacking in the crystal structure following ABCABC)

(see figs. S3 and S4 and section SVI for details). Nanobeam diffraction reveals extra weak reflections (Fig. 2A) along the edge of a hexagonal flake of the electroplated LiCoO_2 , suggesting that the $R\bar{3}m$ symmetry is broken in this region. To further study the crystal microstructure of the electroplated LiCoO_2 and the impurity phases, we adopt the

scanning electron nanobeam diffraction (SEND) technique to investigate a crystal flake with a 3-nm-diameter semi-convergent electron beam (see section SVII for details). The intensities of different reflections $\{hkl\}$ are collected with respect to probe positions (fig. S5). As shown in Fig. 2A, the diffraction patterns obtained from the edge and

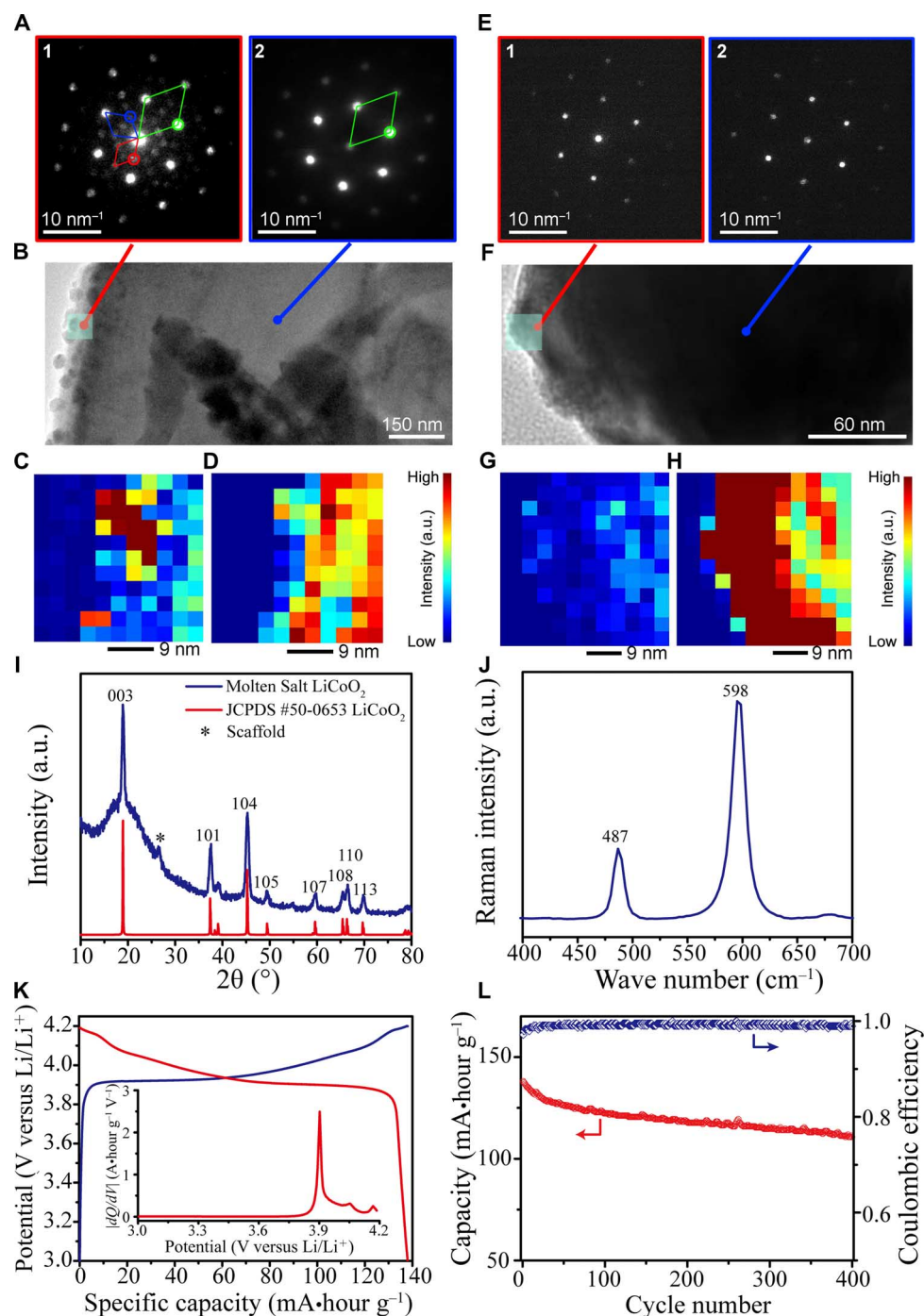


Fig. 2. Characterizations of electroplated LiCoO_2 . (A) Diffraction patterns collected from the edge (1) and center (2) of an as-prepared LiCoO_2 flake and (B) its transmission electron microscopy (TEM) image. Diffraction mapping of (C) non-O3 (intensity multiplied by a factor of 20) and (D) O3 phases. a.u., arbitrary units. (E) Diffraction patterns of spots from the edge (1) and the center (2) of an annealed LiCoO_2 flake and (F) its TEM image. Diffraction patterns of (G) non-O3 (intensity multiplied by a factor of 20) and (H) O3 phases after annealing. XRD (I) and Raman spectroscopy (J) of the LiCoO_2 electrode. (K) Charge/discharge voltage profiles. Inset: $|dQ/dV|$ of the LiCoO_2 cathode (electroplated on an Al foil) versus a lithium electrode. (L) Cycling of the electrodeposited LiCoO_2 cathode versus a Li electrode at 1 C.

the center of the as-synthesized LiCoO_2 flake both show strong $\{110\}$ diffractions belonging to the O3- LiCoO_2 phase (green parallelogram). The additional weak diffractions observed on the edge of the crystal are marked with blue and red circles. The intensities of non-O3 and O3 $\{110\}$ diffractions across the green box in Fig. 2B are mapped with respect to the probe positions in Fig. 2 (C and D), respectively. It appears that there is an ~ 9 -nm non-O3 layer present on the perimeter of a typical ~ 3 - μm crystal flake, consisting of less than 0.06% of the as-deposited material. According to previous reports (25–30), these additional reflections may result from the stack shift, lithium staging/ordering, or a spinel-like intergrowth (fig. S4). The surface phase is most likely related to O2- LiCoO_2 (31, 32). O3- and O2- LiCoO_2 share reflections at 7.08 nm^{-1} , but the O2 structure has extra diffraction spots at 4.12 nm^{-1} because of the ABAC oxygen stacking (33), which is in agreement with the electron diffraction (Fig. 2A). Previous reports have confirmed that O2- LiCoO_2 is thermally unstable and converts to the O3 phase upon annealing at $\sim 400^\circ\text{C}$ (31, 33). After annealing at 400°C in Ar for 2 hours, the edge and center diffraction patterns are similar (Fig. 2, E and F), and the SEND mapping (Fig. 2, G and H) reveals that the diffraction intensity from the non-O3 impurity structure is significantly reduced (the intensity in Fig. 2G is multiplied 20-fold), indicating that the non-O3 impurity phase has been

removed. A more detailed analysis of the possible structures and associated diffraction modeling is in section SVI.

X-ray diffraction (XRD) of the electrodeposited LiCoO_2 (Fig. 2I) agrees with layered LiCoO_2 (space group 166, $R\bar{3}m$). It is notable that the (108) and (110) peaks are split around $\sim 66^\circ$, which has been widely accepted as the evidence of highly crystallized layered LiCoO_2 (25). Raman spectroscopy shows two well-defined peaks at 487 and 598 cm^{-1} (Fig. 2J), corresponding to the E_g and A_{1g} vibration modes of the layered rock-salt LiCoO_2 (34), which is usually only attainable via solid-state reaction at $\sim 900^\circ\text{C}$ (34–36). Figure 2K shows galvanostatic charge/discharge curves of the electroplated LiCoO_2 versus lithium. The well-defined plateaus ($\sim 3.9 \text{ V}$) and the sharp peaks in the dQ/dV curve further confirm that LiCoO_2 has an $R\bar{3}m$ structure with O3 stacking. This plated LiCoO_2 delivers a specific capacity of $138 \text{ mA}\cdot\text{hour g}^{-1}$ from 3 to 4.2 V and retains $\sim 80\%$ of the initial capacity after 400 cycles (Fig. 2L).

The conformal deposition of LiCoO_2 is demonstrated on a conventional Al metal foil current collector and two different carbon scaffolds (see sections SII and SIII for details), a mesoporous carbon foam (Fig. 3D) and a CNF network (Fig. 3G). Figure 3 (A and B) shows the scanning electron microscopy (SEM) images of planar LiCoO_2 films electroplated on both sides of the Al foil. Owing to the excellent

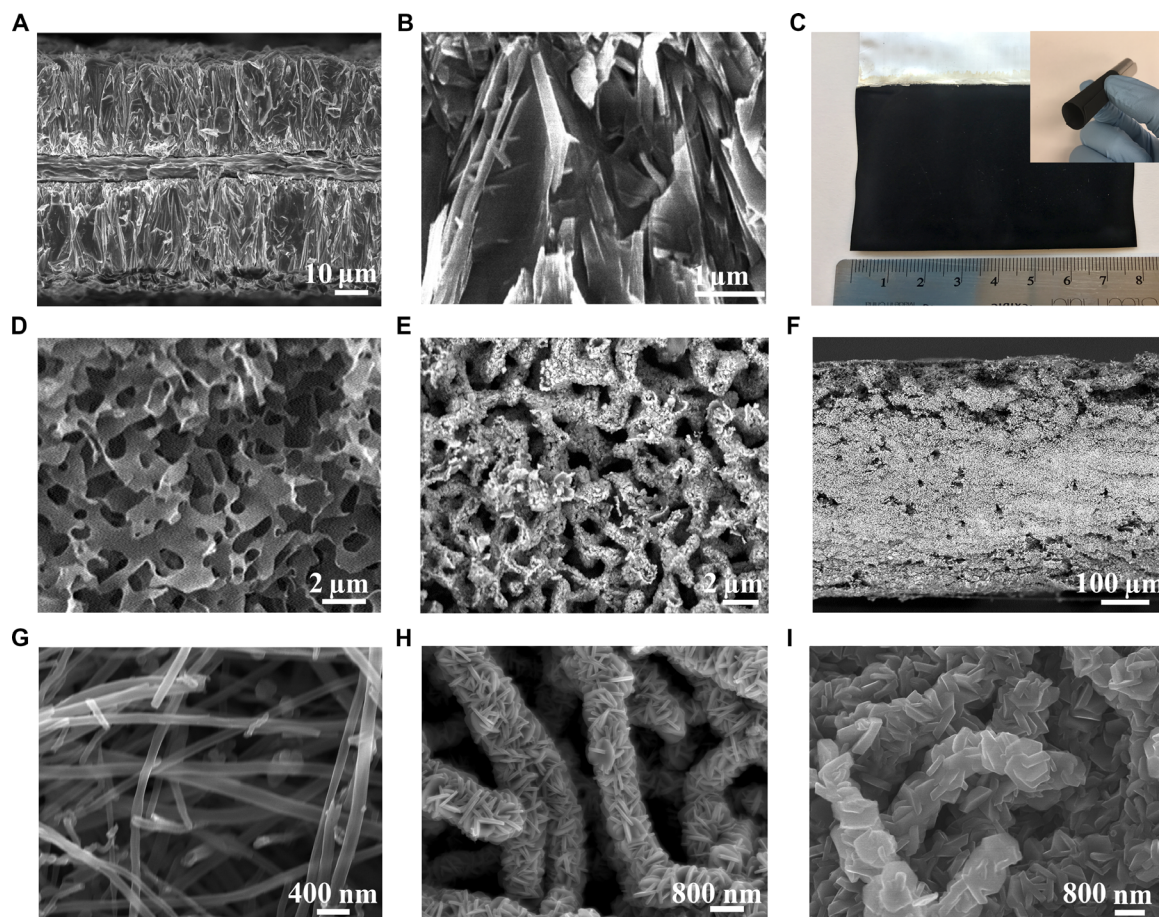


Fig. 3. Morphology of LiCoO_2 electroplated on various substrates. (A) SEM images of planar LiCoO_2 films ($\sim 20\%$ porosity) electroplated on both sides of an Al foil. (B) Higher-magnification view of the LiCoO_2 coating. (C) Optical images of LiCoO_2 electroplated on the Al foil and this electrode rolled into a 5-mm-diameter tube (inset). SEM images of the open-cell carbon foam (D) and the LiCoO_2 /carbon foam electrode (E). (F) Lower-magnification view of a ~ 0.5 -mm-thick LiCoO_2 /carbon foam electrode, with LiCoO_2 plated uniformly throughout the foam. SEM images of the 3D CNF scaffold (G) and the LiCoO_2 electrodes electroplated on this scaffold with $\sim 1 \text{ mA}\cdot\text{hour cm}^{-2}$ loading (H) and $\sim 3 \text{ mA}\cdot\text{hour cm}^{-2}$ loading (I).

electronic conductivity of LiCoO_2 , it is possible to directly grow a nearly 200- μm -thick film (fig. S6). The porosity of the coating, which can be tuned from 10 to 60% by controlling the deposition voltage and duty cycle during the pulsed electroplating, provides the freedom to engineer the electrode flexibility. As demonstrated in Fig. 3C, an appropriate coating porosity ($\sim 20\%$), in conjunction with the strong coating adhesion to the Al foil, enables rolling a $\sim 70\text{-}\mu\text{m}$ -thick electrode (Al foil thickness, 20 μm) at a 5-mm radius. In addition, the high solubility of CoO in the hydroxide melt and the high ionic conductivity of the plating solution minimizes ion depletion during electroplating, allowing uniform deposition of LiCoO_2 throughout thick (0.5 mm) carbon foam scaffolds with an areal loading of $\sim 145\text{ mg cm}^{-2}$ (Fig. 3, E and F). Figure 3 (H and I) shows the SEM images of $\text{LiCoO}_2/\text{CNF}$ electrodes, where the LiCoO_2 coating thickness is tuned by the electrodeposition time.

The intimate contact between the electroplated LiCoO_2 coating and the current collector minimizes the contact resistance, which has been

shown to account for up to 25% of cell polarization in high-power cells (37). We suspect that it is a combination of excellent electrical contact between the LiCoO_2 and the current collector and the high intrinsic electrical conductivity of LiCoO_2 that allows these monolithic electrodes to exhibit excellent power. Figure 4 (A and B) shows the power and cycling performance of a pouch cell consisting of a LiCoO_2/Al foil cathode and a conventional graphite-based anode. The cell retains 75% of the 0.5-C capacity at a 10-C discharge, 55% of the 0.5-C capacity at a 20-C discharge, and $\sim 80\%$ of the initial capacity after 350 cycles, which are impressive results for a cell containing a LiCoO_2 cathode that contains no binders or conductive additives (LiCoO_2 layer is $\sim 25\text{ }\mu\text{m}$ thick and $\sim 80\%$ dense).

When the active material is electroplated on 3D mesostructured current collectors, the power of the resultant electrodes is increased by the improved ion transports in the interconnected pores of the 3D electrode (4). As shown in Fig. 4D, a 100- μm -thick $\text{LiCoO}_2/\text{CNF}$ electrode retains

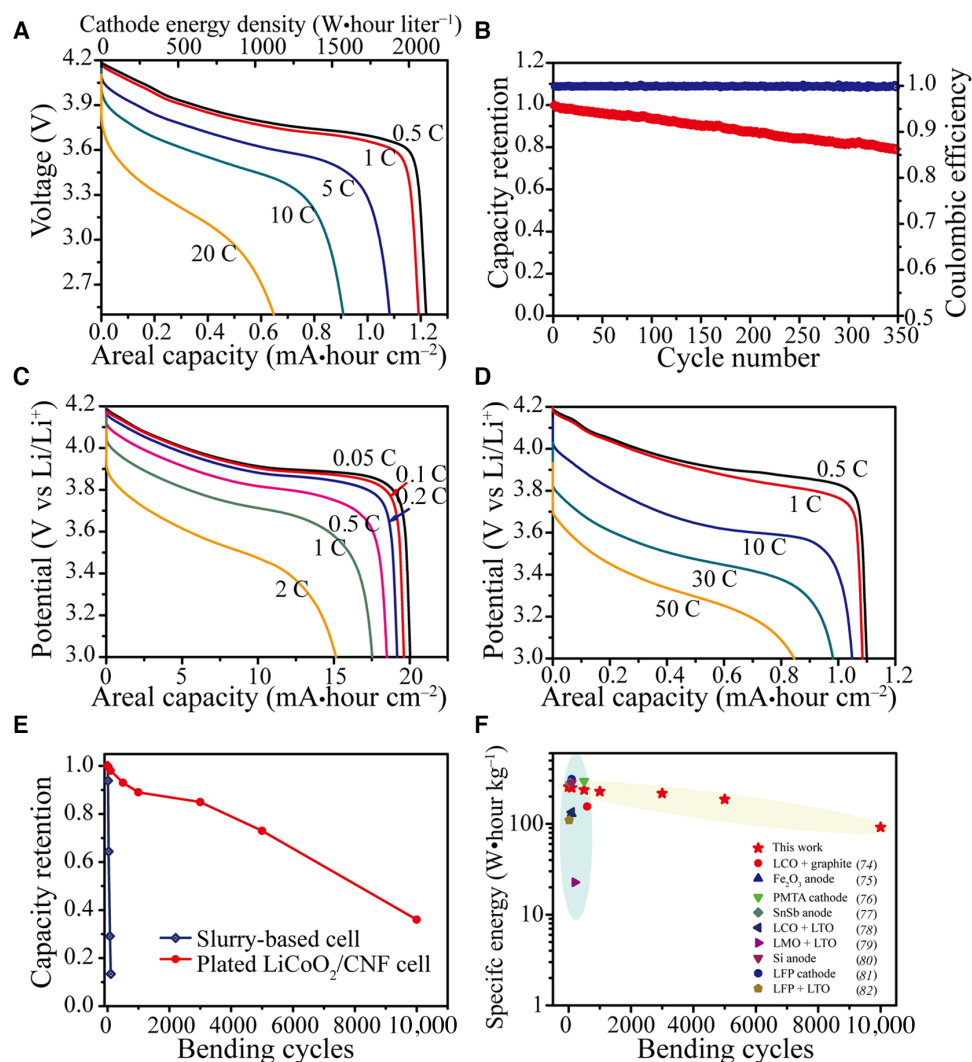


Fig. 4. Electrochemical and flexural properties of LiCoO_2 electrodes. Electrochemical performance of a full pouch cell consisting of a LiCoO_2/Al foil cathode and a conventional anode: (A) capacity retentions of the full cell at varied discharge rates and (B) cycling of the full cell at 1 C. (C) Capacity retentions of a $\sim 20\text{ mA}\cdot\text{hour cm}^{-2}$ $\text{LiCoO}_2/\text{carbon foam}$ electrodes at varied discharge rates. (D) Capacity retentions of a $\sim 1.1\text{ mA}\cdot\text{hour cm}^{-2}$ $\text{LiCoO}_2/\text{CNF}$ electrodes at varied discharge rates. (E) Capacity retention of the $\text{LiCoO}_2/\text{CNF}$ -based and LiCoO_2 slurry-based full cells after cyclic bending of 180° to an $\sim 5\text{-mm}$ radius. (F) Energy density and flexural performance of our and other flexible batteries. LCO, lithium cobalt oxide; PMTA, pyromellitic dianhydride-tris(2-aminoethyl)amine; LTO, lithium titanium oxide; LMO, lithium manganese oxide; LFP, lithium iron phosphate.

90% of the 0.5-C capacity (areal capacity: 1.1 mA-hour cm^{-2}) at a 30-C discharge and $\sim 76\%$ of the 0.5-C capacity at a 50-C discharge. An ~ 0.5 -mm-thick LiCoO_2 /carbon foam electrode delivers ~ 20 mA-hour cm^{-2} at C/5 to C/20 and ~ 15 mA-hour cm^{-2} at 2 C (Fig. 4C), a much better rate capacity relative to other thick electrodes with significantly smaller loadings (38, 39).

Bulk LiCoO_2 is brittle, but, when adhered to the flexible CNF core, it provides a very flexible cathode. We assemble a full cell using a LiCoO_2 /CNF cathode and a graphitized CNF anode. The voltage profiles of the CNF mat and the full cell are shown in figs. S7 and S8. The full cell is bent to an ~ 5 -mm radius at a 180° bending angle (fig. S9) and returned to the flat state. Using an automatic bending machine, the battery demonstrates 70% capacity retention after 5000 bending cycles and 36% retention after 10,000 cycles (Fig. 4E). In contrast, a similar battery containing slurry-cast electrodes or other types of composite electrodes usually fails after tens or hundreds of bending cycles (Fig. 4F). The direct physical and electrical connection of the electrodeposited LTMO to the current collector (figs. S10 and S11) limits delamination and electrical disconnection during bending, which is why we think that this approach provided such a performance after many flexure cycles.

Electrodeposition of LTMOs in molten salt offers a number of unique advantages relative to aqueous, organic, and other molten salt (halides and carbonates) systems. Because the KOH and LiOH eutectic melt is stable over a relatively large potential window and dissolves well the late first row transition metal oxides starting with Mn and several groups of alkaline earth and lanthanide oxides at a relatively low temperature ($\sim 200^\circ\text{C}$), it is possible to produce a diversity of high-valence oxides in a highly crystalline form by applying an electrical potential. As an example showing the generality of the molten hydroxide electrodeposition approach, a spinel LiMn_2O_4 is electrodeposited on a 3D CNF scaffold (fig. S12, A and B) using an electrolyte formed by adding MnO to the LiOH/KOH eutectic melt. Galvanostatic charge/discharge measurements show two well-defined 4-V plateaus (fig. S12C), the signature of high-quality LiMn_2O_4 , that originate from the Li-ion ordering on one-half of the tetrahedral 8a sites (detailed experiment and modeling information are provided in section SIX). Al-doped LiCoO_2 is also synthesized by adding $\text{Al}(\text{OH})_3$ to the CoO -containing plating bath (see section SX for details). Al doping is known to improve both stability and energy density of LiCoO_2 (40, 41).

CONCLUSION

In summary, we present a new and general molten salt electrodeposition method to synthesize high-quality LTMOs at temperatures far below traditional methods. The new fabrication approach enables fabrication of Li-ion batteries with unique form factors and technologically important properties, including high power, high energy, and high flexibility. The inherent advantage of electrodeposition is that it provides conformal growth of active materials in intimate contact with a current collector, providing opportunities to fabricate underdeveloped but urgently desired electrode structures that other techniques are incapable of creating.

MATERIALS AND METHODS

Electroplating LTMOs

The electroplating bath was prepared by mixing KOH and LiOH with a weight ratio of 5:1 in an Ar-filled glove box. It was then heated at 260°C until the mixture became transparent. About 2 weight % CoO (or MnO)

was added into the melt. A Co wire and a Ni plate were used as the reference and the counter electrodes, respectively. During the electroplating, a pulsed waveform was applied between the working and the reference electrodes (1.1-V pulse for 2 s and open-circuit potential for 2 min). We experimentally found that pulsed deposition formed higher-quality material on the planar electrodes than did a constant current or voltage deposition, and pulsed deposition also enabled conformal infilling of the 3D structured electrodes. Depending on the working electrodes, the deposition rate of LTMOs varied from ~ 10 to ~ 100 nm per pulse. After the electrodeposition, the sample was washed with deionized water and dried.

Characterization

The electroplated LTMOs were observed using a Hitachi 4800 SEM. XRD patterns were recorded with a PANalytical X'Pert materials research diffractometer. The high-resolution TEM and the electron diffraction patterns of the electroplated LTMOs were collected with a JEOL Cryo 2100 microscope. Raman spectroscopy was carried out using a Horiba confocal Raman imaging microscope. Coin cells were assembled with Celgard 2700 separator and Novolyte electrolyte (1 M LiPF_6 in a 1:3:1 ratio of ethylene carbonate, dimethylene carbonate, and diethylene carbonate). Flexible cells were assembled within Kapak SealPAK 400 and 500 series heavy-duty pouches (AMPAC Flexibles). The cells were bent using an IPC flexural endurance tester (CK-700FET, Association Connecting Electronics Industries). All electrochemical measurements were performed with a VMP3 multichannel potentiostat (Bio-Logic Corp.).

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at <http://advances.sciencemag.org/cgi/content/full/3/5/e1602427/DC1>

- section SI. Plating bath and solubility of transition metal oxides.
- section SII. Mesoporous carbon foam.
- section SIII. Flexible carbon scaffold.
- section SIV. Quasi-reference electrode.
- section SV. Thermodynamic modeling.
- section SVI. Crystallography of LiCoO_2 .
- section SVII. Scanning electron nanobeam diffraction.
- section SVIII. Flexible battery.
- section SIX. Electrodeposition of spinel LiMn_2O_4 .
- section SX. Electroplating of Al-doped lithium cobalt oxide.
- section SXI. Calculation of energy density of flexible batteries.
- fig. S1. Schematic illustration of a flexible CNF.
- fig. S2. High-resolution TEM images of the CNF.
- fig. S3. High-resolution TEM image and electron diffraction pattern of an electroplated LiCoO_2 crystal flake.
- fig. S4. Crystallographic structures of O3-, O2-, and spinel-phase lithium cobalt oxides and two superstructures with lithium staging and 2×2 periods.
- fig. S5. Illustration of the SEND technique.
- fig. S6. Cross-sectional SEM image of ~ 200 - μm -thick LiCoO_2 electroplated on an Al foil.
- fig. S7. Charge/discharge voltage profiles of the CNF anode.
- fig. S8. Charge/discharge curves of a LiCoO_2 /CNF flexible battery.
- fig. S9. Optical images of bending tests.
- fig. S10. Schematic illustrations of the structure difference between traditional and electroplated flexible batteries.
- fig. S11. SEM images of a LiCoO_2 /CNF cathode before and after 1000 bending cycles.
- fig. S12. Materials and electrochemical characterization of the electroplated LiMn_2O_4 /CNF battery.
- fig. S13. The Gibbs free energy of the formation from the elements for LiMn_2O_4 .
- fig. S14. The Gibbs free energy of LiMn_2O_4 .
- fig. S15. The potential- pH_2O diagram of the LiOH-KOH-MnO- H_2O melt system.
- fig. S16. Materials and electrochemical characterization of the electroplated Al-doped LiCoO_2 .
- table S1. Thermodynamic data used for the LiOH-KOH- CoO system at 260°C .
- table S2. Thermodynamic data of the LiOH-KOH-MnO system at 25°C .

table S3. Thermodynamic data of the LiOH-KOH-MnO system at 300°C.

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