ELECTROPLATING

Electroplating lithium transition metal oxides

Huigang Zhang,1* Hailong Ning,2* John Busbee,2 Zihan Shen,1 Chadd Kiggins,2 Yuyan Hua,2 Janna Eaves,2 Jerome Davis III,2 Tan Shi,2 Yu-Tsun Shao,3 Jian-Min Zuo,3,4 Xuhao Hong,1 Yanbin Chan,1 Shuangbao Wang,1 Peng Wang,1 Pengcheng Sun,3 Sheng Xu,5 Jinyun Liu,3 Paul V. Braun2,3,4,6,7,*

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°C 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°C 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 valence 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°C to 1000°C) routes. This method is compatible with a variety of conventional (for example, Al foil) and mesostructured 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 SI) 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.
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-$p$H$_2$O diagram (Pourbaix diagram). In a hydroxide melt, H$_2$O acts as a Lux-Flood acid and accepts O$^{2-}$, turning into 2OH$^-$. The acidity, $p$H$_2$O [defined as $-\log(\chi_{\text{H}_2\text{O}})$], 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$_3$O$_4$ is thermodynamically favorable because of the low formation potential ($\sim$23, 24). As the melt becomes more basic, Co$_3$O$_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 O$_3$-LiCoO$_2$ (O$_3$ refers to the oxygen stacking in the crystal structure following ABCABC).
Nanobeam diffraction reveals extra weak reflections (Fig. 2A) along the edge of a hexagonal flake of the electroplated LiCoO$_2$, suggesting that the R$3\text{m}$ symmetry is broken in this region. To further study the crystal microstructure of the electroplated LiCo$_2$ 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 center of the flake are different, indicating a non-uniform crystal microstructure. The transmission electron microscopy (TEM) images (Fig. 2B) also show the flake's thickness and the presence of different phases. Diffraction mapping of non-O$_3$ (Fig. 2C) and O$_3$ phases (Fig. 2D) further confirm the phase distribution. The diffraction patterns of spots from the edge (1) and the center (2) of an annealed LiCoO$_2$ flake are shown in Fig. 2E and F, respectively, and the TEM image in Fig. 2F. The XRD and Raman spectroscopy of the LiCoO$_2$ electrode are shown in Fig. 2I and J, respectively. The charge/discharge voltage profiles of the electrodeposited LiCoO$_2$ cathode (electroplated on an Al foil) versus a lithium electrode are shown in Fig. 2K. Cycling of the electrodeposited LiCoO$_2$ cathode versus a Li electrode at 1 C is shown in Fig. 2L.
the center of the as-synthesized LiCoO₂ flake both show strong {110} diffractions belonging to the O₃-LiCoO₂ 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 a ~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-LiCoO₂ (31, 32). O₃- and O₂-LiCoO₂ 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-LiCoO₂ is thermally unstable and converts to the O₃ phase upon annealing at ~400°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 LiCoO₂ (Fig. 2I) agrees with layered LiCoO₂ (space group 166, R̅3m). It is notable that the (108) and (110) peaks are split around ~66°, which has been widely accepted as the evidence of highly crystallized layered LiCoO₂ (25). Raman spectroscopy shows two well-defined peaks at 487 and 598 cm⁻¹ (Fig. 2J), corresponding to the E₉ and A₁₉ vibration modes of the layered rock-salt LiCoO₂ (34), which is usually only attainable via solid-state reaction at ~900°C (34–36). Figure 2K shows galvanostatic charge/discharge curves of the electroplated LiCoO₂ versus lithium. The well-defined plateaus (~3.9 V) and the sharp peaks in the dQ/dV curve further confirm that LiCoO₂ has an R̅3m structure with O₃ stacking. This plated LiCoO₂ delivers a specific capacity of 138 mA·hour g⁻¹ from 3 to 4.2 V and retains ~80% of the initial capacity after 400 cycles (Fig. 2L).

The conformal deposition of LiCoO₂ 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 LiCoO₂ films electroplated on both sides of the Al foil. Owing to the excellent
electronic conductivity of LiCoO₂, 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 (~20%), in conjunction with the strong coating adhesion to the Al foil, enables rolling a ~70-μm-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 LiCoO₂ throughout thick (0.5 mm) carbon foam scaffolds with an areal loading of ~145 mg cm⁻² (Fig. 3, E and F). Figure 3 (H and I) shows the SEM images of LiCoO₂/CNF electrodes, where the LiCoO₂ coating thickness is tuned by the electrodeposition time.

The intimate contact between the electroplated LiCoO₂ 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 LiCoO₂ and the current collector and the high intrinsic electrical conductivity of LiCoO₂ 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 LiCoO₂/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 ~80% of the initial capacity after 350 cycles, which are impressive results for a cell containing a LiCoO₂ cathode that contains no binders or conductive additives (LiCoO₂ layer is ~25 μm thick and ~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 LiCoO₂/CNF electrode retains

---

**Fig. 4.** Electrochemical and flexural properties of LiCoO₂ electrodes. Electrochemical performance of a full pouch cell consisting of a LiCoO₂/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 ~20 mA·hour cm⁻² LiCoO₂/carbon foam electrodes at varied discharge rates. (D) Capacity retentions of a ~1.1 mA·hour cm⁻² LiCoO₂/CNF electrodes at varied discharge rates. (E) Capacity retention of the LiCoO₂/CNF-based and LiCoO₂ slurry–based full cells after cyclic bending of 180° to an ~5-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 ~76% of the 0.5-C capacity at a 50-C discharge. An ~0.5-mm-thick LiCoO₂/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 LiCoO₂ is brittle, but, when adhered to the flexible CNF core, it provides a very flexible cathode. We assemble a full cell using a LiCoO₂/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 (~200°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 LiMn₂O₄ is electrodeposited on a 3D CNF scaffold (fig. S12A 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 LiMn₂O₄ 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 LiCoO₂ is also synthesized by adding Al(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 LiCoO₂ (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 XPert 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 LiPF₆ in a 1:3:1 ratio of ethylene carbonate, dimethylene carbonate, and diethyl 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 LiCoO₂.
section SVII. Scanning electron nanobeam diffraction.
section SVIII. Flexible battery.
section SIX. Electrodeposition of spinel LiMn₂O₄.
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 LiCoO₂ crystal flake.
fig. S4. Crystallographic structures of O₃, O₂, and spinel-phase lithium cobalt oxides and two superstructures with lithium staking and 2 × 2 periods.
fig. S5. Illustration of the SEND technique.
fig. S6. Cross-sectional SEM image of ~200-μm-thick LiCoO₂ electroplated on an Al foil.
fig. S7. Charge/discharge voltage profiles of the CNF anode.
fig. S8. Charge/discharge curves of a LiCoO₂/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 LiCoO₂/CNF cathode before and after 1000 bending cycles.
fig. S12. Materials and electrochemical characterization of the electroplated LiMn₂O₄/CNF battery.
fig. S13. The Gibbs free energy of the formation from the elements for LiMn₂O₄.
fig. S14. The Gibbs free energy of LiMn₂O₄.
fig. S15. The potential-pH diagram of the LiOH-KOH-MnO-H₂O melt system.
fig. S16. Materials and electrochemical characterization of the electroplated Al-doped LiCoO₂.
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.
REFERENCES AND NOTES


11. J. Liu, X. Sun, Elegant design of electrode and electrode/electrolyte interface in lithium-ion batteries by atomic layer deposition. Nanotechnology 26, 024001 (2015).


21. W.-S. Yoon, K.-K. Lee, K.-B. Kim, Structural and electrochemical properties of LiNi0.5Co0.5O2 cathode for Li rechargeable batteries. J. Electrochem. Soc. 147, 2023–2028 (2000).


30. A. Van der Ven, M. K. Aydinol, G. Ceder, First-principles evidence for stage ordering in Li2CO3-Li3PO4-LiAlO2 electrolyte and LiCoO2-Co3O4 as solid reference electrode. J. Electrochem. Soc. 162, A1236–A1246 (2010).


Acknowledgments: H.Z. thanks H. Chen (Georgia Tech) for the insightful discussions. Funding: Work at the University of Illinois Urbana Champaign is supported by the Basic Energy Sciences, Office of Science, U.S. Department of Energy, under award DE-FG02-07ER46741. Work at Nanjing University is supported by the Thousand Youth Talents Plan (no. 128010), the National Materials Genome Project (2016YFB0700600), the Jiangsu Outstanding Young Funds (BK20160012), and the “Jiangsu Shaunghuang” Program. S.W. and P.V.B. acknowledge the support from the National Natural Science Foundation of China (11474147), the National Basic Research Program of China (2015CB654901). We thank the High Performance Computing Center of Nanjing University for numerical calculations. Author contributions: H.Z. conceived the first successful bath chemistry. H.Z., H.N., and P.V.B. built off this discovery and supervised the work. H.Z., H.N., and J.B. supervised the materials synthesis. C.K., Y.H., J.E., J.D., T.S., and S.W. performed electrochemical and mechanical characterizations. Y.T.S., J.M.Z., X.H., Y.C., S.W., and J.L. performed material characterizations and assisted in the interpretation of results. H.Z., H.N., and P.V.B. wrote the manuscript. All authors have discussed the results and commented on the manuscript. Competing interests: P.V.B has an equity stake in and is a co-founder, the chief technology officer, and a member of the Board of Directors of Xerion Advanced Battery Corp. H.N. is an employee of Xerion Advanced Battery Corp. J.B. is a shareholder and the chief executive officer of Xerion Advanced Battery Corp. J.E. is an employee of Xerion Advanced Battery Corp. Xerion Advanced Battery Corporation has an application for a patent related to this work. US 2016/0028081 A1 (application no. 14/806,066, filed on 22 July 2015). Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors. Samples and characterization data are archived and can be made available upon request.

Submitted 3 October 2016 Accepted 22 March 2017 Published 12 May 2017 10.1126/sciadv.1602427

Electroplating lithium transition metal oxides


Sci Adv 3 (5), e1602427.
DOI: 10.1126/sciadv.1602427