

# Transparent lithium-ion batteries

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Transparent devices have recently attracted substantial attention. Various applications have been demonstrated, including displays, touch screens, and solar cells; however, transparent batteries, a key component in fully integrated transparent devices, have not yet been reported. As battery electrode materials are not transparent and have to be thick enough to store energy, the traditional approach of using thin films for transparent devices is not suitable. Here we demonstrate a grid-structured electrode to solve this dilemma, which is fabricated by a microfluidics-assisted method. The feature dimension in the electrode is below the resolution limit of human eyes, and, thus, the electrode appears transparent. Moreover, by aligning multiple electrodes together, the amount of energy stored increases readily without sacrificing the transparency. This results in a battery with energy density of 10 Wh/L at a transparency of 60%. The device is also flexible, further broadening their potential applications. The transparent device configuration also allows in situ Raman study of fundamental electrochemical reactions in batteries.

energy storage | flexible electronics | self-assembly | transparent electronics

Transparent electronics is an emerging and promising technology for the next generation of optoelectronic devices. Transparent devices have been fabricated for various applications, including transistors (1–6), optical circuits (7), displays (8–10), touch screens (11), and solar cells (12–14). However, the battery, a key component in portable electronics, has not been demonstrated as a transparent device. Consequently, fully integrated and transparent devices cannot be realized because the battery occupies a considerable footprint area and volume in these devices (e.g., cell phones and tablet computers). Typically, a battery is composed of electrode materials, current collectors, electrolyte, separators, and packaging (15). None of them are transparent except for the electrolyte. Furthermore, as these components are in series, all of them must be clear to make the whole device transparent. A widely used method for making transparent devices is to reduce the thickness of active materials down to much less than their optical absorption length, as demonstrated in carbon nanotubes (5, 7), graphene (11), and organic semiconductors (12, 14). However, this approach is not suitable for batteries, because, to our knowledge, no battery material has an absorption length long enough in the full voltage window. For example, LiCoO<sub>2</sub> and graphite, the most common cathode and anode in Li-ion batteries, are good absorbers even with a thickness less than 1 μm. Moreover, black conductive carbon additive is always required in electrodes, which occupies at least 10% of the total volume (16). In contrast, to power common portable electronics, the total thickness of electrode material needs to be on the order of 100 μm–1 mm, much longer than the absorption length of electrode materials. This dilemma comes from the fact that the transparency of materials decays exponentially with the thickness, whereas the amount of energy stored increases only linearly with the thickness. Some transparent materials, such as indium oxide (In<sub>2</sub>O<sub>3</sub>), could be used as battery materials. However, upon cycling, metal nanoparticles and lithium oxides are formed, significantly deteriorating the transparency (Figs. S1 and S2) (17). To overcome these challenges, we demonstrate a unique microfluidics-assisted method to make a patterned grid-like battery elec-

trode filled with nanomaterials. The battery appears transparent as the patterned electrode materials cover only a small portion of the whole area and the pattern features are smaller than the detection limit of human eyes. Li-ion batteries with different transparencies were fabricated. For example, a full cell with an energy density of 10 Wh/L, including packaging, is demonstrated at a transparency of 60%. Furthermore, by aligning multiple transparent batteries in series, the energy stored could scale up easily without sacrificing the transparency of the device. Finally, we show that such a device is also a powerful tool for in situ optical studies of electrochemical reactions in batteries.

## Results

**Design and Fabrication of Transparent Li-Ion Batteries.** To circumvent the intrinsic problem of the opacity of battery electrode materials, we utilize a previously undescribed strategy of designing patterned electrodes with very small features so that the nontransparent materials cover only a small portion of the whole area of the device, as illustrated in Fig. 1A. The opaque battery electrode materials (black) and metal current collectors (yellow) beneath are confined inside the grid, whereas the rest of the electrode substrate is transparent. If the feature dimension of the lines is comparable or less than the resolution of human eyes (50–100 μm), the opaque electrode grid is indistinguishable from the transparent substrate. Consequently, the entire device appears transparent. At a transparency of  $\alpha$ , the areal portion of opaque electrode materials is  $1 - \alpha$ . Moreover, by aligning multiple layers of electrodes together, the transparency does not decrease, whereas the energy stored increases linearly. In contrast, the transparency of thin film electrodes decreases exponentially when more cells are stacked in series (18, 19). As a result, a transparent battery with practical capacity for portable electronics can be accomplished using patterned electrodes on clear substrates. Fig. 1B plots the calculated transparency versus volumetric energy density of such devices. The theoretical limit based on only active materials is shown in black, whereas the red line considers the volume of all other components in a battery, including current collectors, separators, and packaging. At a transparency of 60%, the theoretical energy density is about 100 Wh/L with packaging, which is comparable to the energy density of lead acid and NiCd rechargeable batteries (see *SI Text*) (15). By varying the width and space in the grid, we fabricate batteries with transparency of 30%, 60%, and 78%, as indicated by the green triangles in Fig. 1B. The corresponding energy density is 20, 10, and 5 Wh/L considering packaging, which proves the feasibility of this approach.

The concept of patterned electrodes is an effective method to fabricate transparent batteries. However, realizing such a structure is not trivial, especially for batteries. The battery electrode is a thick porous film (typically 30–300 μm), composed of heterogeneous powders with entirely different properties: inorganic

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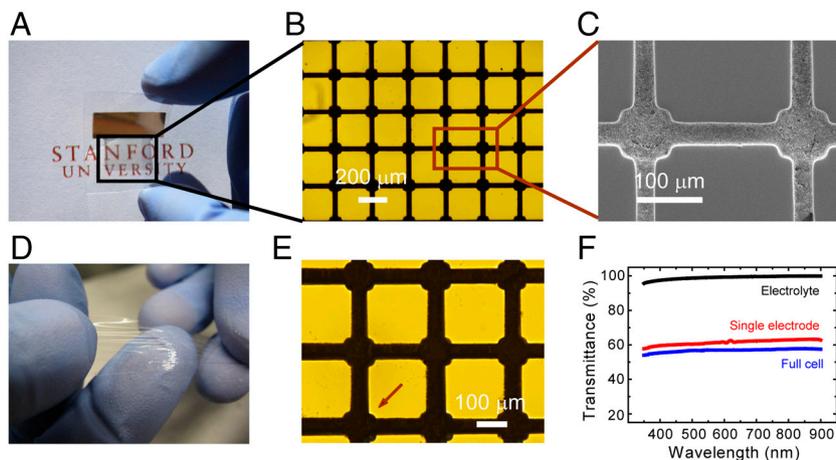
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**Fig. 2.** (A) Photographic image of a transparent and flexible battery electrode. (B and C) Magnified optical image (B) and SEM image (C) of the battery electrode. Electrode materials are only confined inside the trenches. (D) Transparent, flexible, and stretchable gel electrolyte. (E) Optical microscopic image of a full battery with electrodes matched to each other. A small mismatch (*Bottom Left*) is marked by the red arrow. (F) The UV-VIS spectrum of gel electrolyte, a single electrode, and a full battery.

ergy at the same time. This is accomplished by matching the electrodes manually under a microscope, but can be achieved automatically in the future. Fig. 2E shows an optical image of an assembled transparent Li-ion battery with two electrodes and a gel electrolyte membrane in between. It is clear that the two electrodes align well with each other and only a small mismatch is observed at the bottom left corner.

**Transparency Measurement.** To quantitatively study the transparency of battery components and the full device, UV-visible (UV-VIS) spectroscopy is used to measure the transmittance of each component, as plotted in Fig. 2F. The gel electrolyte exhibits transmittance of about 99%, so its effect on the transparency of the full battery is negligible. A single electrode without packaging showed a transmittance of 62% in the visible and near infrared, which is 3% lower than the theoretical value based on the area of battery materials in the design. The difference may originate from the coverage area of the battery material, but could also occur because the UV-VIS spectrum only measures the direct transmittance, but not the diffuse transmittance. The full cell with packaging exhibits a transmittance of 57%. The 5% difference in transmittance between a single electrode and a full cell is likely a result of the small mismatch (3–5  $\mu\text{m}$ ) between the two electrodes, which is consistent with observations from optical microscopy images (Fig. 2E), or a small amount of absorption from the packaging. Nevertheless, the transmittance of the full cell is much higher than two electrodes randomly stacked (0.652~42%). When more electrodes are stacked together, the difference will be even more significant. For example, a device with three full cells in series will exhibit a transparency less than 10% if they are randomly oriented. In contrast, well-aligned cells show transparency similar to an individual electrode (approximately 60%).

**Electrochemical Characterizations.** Before investigating the performance of the transparent battery, the electrochemical behavior of each component was examined first. PDMS and gold are not used in traditional batteries. PDMS has been previously reported as a component in a copolymer electrolyte (27). Gold is inert in the range of 1.0–4.4 V versus Li/Li<sup>+</sup> (28, 29), in which the operating potential range of the chosen cathode (3.5–4.25 V versus Li/Li<sup>+</sup> for LiMn<sub>2</sub>O<sub>4</sub>) and anode (1.3–1.8 V Li/Li<sup>+</sup> for Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>) lie. To further test the stability of the gold film on PDMS, cyclic voltammetry was performed, showing little reaction with lithium in the potential window (Fig. S4). A small anodic peak is observed at 2.1 V, but it disappears after several scans. This indicates that the initial Coulomb efficiency might be slightly

low at the anode side (Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>). However, the current density is less than 10  $\mu\text{A}/\text{cm}^2$  at 2 mV/s, which is much less than the current used in charging/discharging batteries (100  $\mu\text{A}/\text{cm}^2$ ). Furthermore, because the peak diminishes quickly upon scanning and does not remain within the potential window for the full cell, this side reaction has little effect on battery performance after the first cycle. This argument is also supported by full cell cycling data discussed later in this paper.

Fig. 3A exhibits the typical voltage profiles of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> nanopowder and LiMn<sub>2</sub>O<sub>4</sub> nanorods, respectively. The profiles are similar to those observed in conventional battery electrode (24, 30), and no significant overpotential is observed. To quantitatively understand how the grid design affects the voltage profile, we measured the resistance of the transparent electrodes. The sheet resistance is approximately 60  $\Omega/\text{sq}$  for both electrodes, suggesting an additional overpotential of only 3 mV in half cells at 100  $\mu\text{A}/\text{cm}^2$ . The electrode is also flexible. Even after repeatedly bending down to a radius of 2 cm 100 times, the sheet resistance is still less than 100  $\Omega/\text{sq}$ . After bending, only a slightly higher overpotential is observed and the corresponding capacity is less than 5% lower than before bending (Fig. 3A, dashed line). Resistances of the electrode bent to different radii are measured and no dramatic change is observed at radii above 1 cm (Fig. S5). We attribute the good flexibility of transparent electrodes to two reasons: (i) the flexibility of PDMS and (ii) conductive carbon black can bridge cracked Au electrode pieces. The cycling performance of these transparent electrodes is shown in Fig. 3B. The LiMn<sub>2</sub>O<sub>4</sub> nanorod and Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> nanopowder electrodes showed initial discharge capacities of 97 mAh/g and 142 mAh/g and capacity retentions of 87% and 93% after 40 cycles at 100  $\mu\text{A}/\text{cm}^2$ , respectively. To derive the specific capacity, the mass loading is calculated based on the tapping density and the thickness of the electrode film. The tapping density is estimated from electrode films with the same composition coated by doctor blading with the same composition, which is 1.1 g/cm<sup>3</sup> for LiMn<sub>2</sub>O<sub>4</sub> and 1.2 g/cm<sup>3</sup> for Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> electrodes, respectively. As a result, the estimated mass loading is 1.8 mg/cm<sup>2</sup> for LiMn<sub>2</sub>O<sub>4</sub> and 1.9 mg/cm<sup>2</sup> for Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>, which leads to specific capacity consistent with previous reports (20, 24, 30). The Coulomb efficiency is above 97% for both electrodes. Passivation of PDMS with transparent materials (e.g., polymer or oxides) could further improve the Coulomb efficiency. Impedance measurements show that the transparent gel electrolyte has an ionic conductivity of  $2 \times 10^{-3}$  S/cm, which satisfies the requirement for commercial batteries (Fig. S6).



the feasibility of using a transparent battery for an in situ optical spectroscopy study of fundamental electrochemical reactions.

## Discussion

The theoretical energy density with packaging is 100 Wh/L, about one order of magnitude higher than the transparent battery demonstrated. The difference mainly comes from a thick PDMS substrate (approximately 100  $\mu\text{m}$ ) and thin electrode film (approximately 50  $\mu\text{m}$ ). With further optimization, including reducing the thickness of PDMS substrate, increasing the depth of the trenches and using materials with higher specific capacity and tapping density (e.g.,  $\text{LiCoO}_2$ ), we believe that the energy density could be increased to over 50 Wh/L.

Moreover, in some types of portable electronics and miniaturized devices, the footprint area is limited, but the restriction on device thickness is less stringent. As a result, the energy per area is more important than the energy per volume for certain applications (33, 34). Given the opportunity to stacking multiple cells in series, which increases the areal energy density without sacrificing the transparency, our unique electrode grid design is favorable to thin film designs and will result in practical transparent batteries.

In this paper, we have proposed and realized an approach to pattern battery electrodes at the micron scale to fabricate transparent batteries, which can function as the power supply in transparent electronics. As the feature size of the patterned electrode is less than the resolution of human eyes, the nontransparent electrode materials cannot be distinguished from the transparent PDMS substrate, resulting in a transparent electrode. The grid-like structure of the electrode is achieved through a unique method based on microfluidic techniques, which allows us to fabricate battery electrodes with a well-defined grid structure. Furthermore, by aligning multiple electrodes together, the transparency does not decrease, whereas the energy stored in the battery increases linearly with the number of electrodes. The as-fabricated devices show transparency of 78, 60, and 30% and corresponding energy density of 5, 10, and 20 Wh/L with packaging.

## Materials and Methods

**Materials.**  $\text{LiMn}_2\text{O}_4$  is synthesized by annealing a mixture of  $\beta\text{-MnO}_2$  nanorods and lithium acetate (20), and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  powders are from Hydro-Québec. To make gel electrolyte, 1 M  $\text{LiClO}_4$  in EC/DEC and PVDF-HFP is first dissolved in tetrahydrofuran. After stirring, the clear solution is drop cast onto a glass slide and dried to remove tetrahydrofuran. The membrane is soaked in 1 M  $\text{LiClO}_4$  in EC/DEC after drying.

- Sanghyun J, et al. (2007) Fabrication of fully transparent nanowire transistors for transparent and flexible electronics. *Nat Nanotechnol* 2:378–384.
- Yu GH, Cao AY, Lieber CM (2007) Large-area blown bubble films of aligned nanowires and carbon nanotubes. *Nat Nanotechnol* 2:372–377.
- Cao Q, et al. (2006) Highly bendable, transparent thin-film transistors that use carbon-nanotube-based conductors and semiconductors with elastomeric dielectrics. *Adv Mater* 18:304–309.
- Lian W, et al. (2006) High-performance transparent inorganic-organic hybrid thin-film n-type transistors. *Nat Mater* 5:893–900.
- Artukovic E, Kaempgen M, Hecht DS, Roth S, Gruner G (2005) Transparent and flexible carbon nanotube transistors. *Nano Lett* 5:757–760.
- Nomura K, et al. (2003) Thin-film transistor fabricated in single-crystalline transparent oxide semiconductor. *Science* 300:1269–1272.
- Wu ZC, et al. (2004) Transparent, conductive carbon nanotube films. *Science* 305:1273–1276.
- Park SI, et al. (2009) Printed assemblies of inorganic light-emitting diodes for deformable and semitransparent displays. *Science* 325:977–981.
- Ju S, et al. (2008) Transparent active matrix organic light-emitting diode displays driven by nanowire transistor circuitry. *Nano Lett* 8:997–1004.
- Gorrn P, et al. (2006) Towards see-through displays: Fully transparent thin-film transistors driving transparent organic light-emitting diodes. *Adv Mater* 18:738–741.
- Bae S, et al. (2010) Roll-to-roll production of 30-inch graphene films for transparent electrodes. *Nat Nanotechnol* 5:574–578.
- Lee JY, Connor ST, Cui Y, Peumans P Semitransparent organic photovoltaic cells with laminated top electrode. *Nano Lett* 10:1276–1279.
- Yoon J, et al. (2008) Ultrathin silicon solar microcells for semitransparent, mechanically flexible and microconcentrator module designs. *Nat Mater* 7:907–915.
- Huang JS, Li G, Yang Y (2008) A semi-transparent plastic solar cell fabricated by a lamination process. *Adv Mater* 20:415–419.

**Fabrication of Transparent Battery.** PDMS substrate with grid trenches is fabricated by spin coating PDMS precursor (Sylgard 184) onto a silicon mold patterned by photolithography. The PDMS film is cured at 80 °C and peeled off from the mold. After 100 nm gold is evaporated onto PDMS as the current collector, the substrate surface is made hydrophilic by air plasma. Then the electrode material solution is filled in by a microfluidics-assisted method. The electrode material is composed of 90% active materials ( $\text{LiMn}_2\text{O}_4$  or  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ), 7% carbon black, and 3% aqueous binder (Pred materials). The concentration of solid materials in the solution is 18–20%.

To introduce the slurry solution to the predesigned trenches, a thin slide of PDMS is placed at one end of the electrode region to form an area of closed channels. Then the slurry solution is dropped onto one side of the channels. Because of the capillary force, the aqueous solution is sucked into channels under the blocking PDMS and then continues flowing in the channels not covered by PDMS. The flowing speed is about 1 cm/s. Then the solution is dried and the blocking PDMS piece is removed. Finally, a piece of Kapton tape is carefully pressed onto the PDMS substrate and extra gold film is peeled off.

To make a full cell, aluminum strip is wrapped onto the side of each electrode. Then, gel electrolyte is placed on the anode electrode first, and the transparent cathode is put on the anode under optical microscope at 20 $\times$ . The full cell is sealed inside a highly transparent poly(vinyl chloride) (PVC) thermoplastic bag with metal current collector extending out. The cell configuration is very similar to a pouch cell except that all components are transparent.

**Electrochemical Measurement.** Half cell is made by sealing the electrode in transparent plastic bags in a glove box. Lithium foil is used as the counter electrode in half cells and the electrolyte is the transparent gel membrane. For full cell tests, the gel electrolyte membrane is sandwiched between two transparent electrodes. Then the full cell is packed in transparent plastic bags. Cyclic voltammetry is performed in a three-electrode configuration, where both counter and reference electrode are lithium. PVC sealing bags are used in all electrochemical tests.

**Transmittance Test.** UV-VIS spectroscopy is used to measure the transmittance of samples. A glass slide is used as the reference. For half cell and gel electrolyte, packaging is not included, whereas the transparency of full cell is measured with packaging.

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- Tarascon JM, Armand M (2001) Issues and challenges facing rechargeable lithium batteries. *Nature* 414:359–367.
- Hong JK, Lee JH, Oh SM (2002) Effect of carbon additive on electrochemical performance of  $\text{LiCoO}_2$  composite cathodes. *J Power Sources* 111:90–96.
- Ho WH, Li CF, Liu HC, Yen SK (2008) Electrochemical performance of  $\text{In}_2\text{O}_3$  thin film electrode in lithium cell. *J Power Sources* 175:897–902.
- Chen PC, Shen G, Sukcharoenchoke S, Zhou C (2009) Flexible and transparent supercapacitor based on  $\text{In}_2\text{O}_3$  nanowire/carbon nanotube heterogeneous films. *Appl Phys Lett* 94:043113.
- Martin F, et al. (2010) High-energy, efficient and transparent electrode for lithium batteries. *J Mater Chem* 20:2847–2852.
- Yang Y, et al. (2009) Single nanorod devices for battery diagnostics: A case study on  $\text{LiMn}_2\text{O}_4$ . *Nano Lett* 9:4109–4114.
- Kang B, Ceder G (2009) Battery materials for ultrafast charging and discharging. *Nature* 458:190–193.
- Gates B, Qin D, Xia YN (1999) Assembly of nanoparticles into opaline structures over large areas. *Adv Mater* 11:466–469.
- Kim E, Xia YN, Whitesides GM (1996) Two- and three-dimensional crystallization of polymeric microspheres by micromolding in capillaries. *Adv Mater* 8:245–247.
- Kim DK, et al. (2008) Spinel  $\text{LiMn}_2\text{O}_4$  nanorods as lithium ion battery cathodes. *Nano Lett* 8:3948–3952.
- Xue MQ, et al. (2009) Transfer printing of metal nanoparticles with controllable dimensions, placement, and reproducible surface-enhanced raman scattering effects. *Langmuir* 25:4347–4351.
- Arora P, Zhang ZM (2004) Battery separators. *Chem Rev* 104:4419–4462.
- Bouridah A, Dalard F, Deroo D, Cheradame H, Lenest JF (1985) Poly(dimethylsiloxane)-poly(ethylene oxide) based polyurethane networks used as electrolytes in lithium electrochemical solid-state batteries. *Solid State Ionics* 15:233–240.
- Mui SC, et al. (2002) Block copolymer-templated nanocomposite electrodes for rechargeable lithium batteries. *J Electrochem Soc* 149:A1610–A1615.

29. Lim MR, Cho WI, Kim KB (2001) Preparation and characterization of gold-codeposited  $\text{LiMn}_2\text{O}_4$  electrodes. *J Power Sources* 92:168–176.
30. Zaghbi K, Simoneau M, Armand M, Gauthier M (1999) Electrochemical study of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  as negative electrode for Li-ion polymer rechargeable batteries. *J Power Sources* 81–82:300–305.
31. Amundsen B, Burns GR, Islam MS, Kanoh H, Roziere J (1999) Lattice dynamics and vibrational spectra of lithium manganese oxides: A computer simulation and spectroscopic study. *J Phys Chem B* 103:5175–5180.
32. Huang WW, Frech R (1999) In situ Raman spectroscopic studies of electrochemical intercalation in  $\text{Li}_x\text{Mn}_2\text{O}_4$ -based cathodes. *J Power Sources* 81–82:616–620.
33. Long JW, Dunn B, Rolison DR, White HS (2004) Three-dimensional battery architectures. *Chem Rev* 104:4463–4492.
34. Baggetto L, Roozeboom F, Niessen RAH, Notten PHL (2008) On the route toward 3D-integrated all-solid-state micro-batteries. *Solid State Technol* 51:30–35.