

# Simple battery armor to protect against gastrointestinal injury from accidental ingestion

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**Inadvertent battery ingestion in children and the associated morbidity and mortality results in thousands of emergency room visits every year. Given the risk for serious electrochemical burns within hours of ingestion, the current standard of care for the treatment of batteries in the esophagus is emergent endoscopic removal. Safety standards now regulate locked battery compartments in toys, which have resulted in a modest reduction in inadvertent battery ingestion; specifically, 3,461 ingestions were reported in 2009, and 3,366 in 2013. Aside from legislation, minimal technological development has taken place at the level of the battery to limit injury. We have constructed a waterproof, pressure-sensitive coating, harnessing a commercially available quantum tunneling composite. Quantum tunneling composite coated (QTCC) batteries are nonconductive in the low-pressure gastrointestinal environment yet conduct within the higher pressure of standard battery housings. Importantly, this coating technology enables most battery-operated equipment to be powered without modification. If these new batteries are swallowed, they limit the external electrolytic currents responsible for tissue injury. We demonstrate in a large-animal model a significant decrease in tissue injury with QTCC batteries compared with uncoated control batteries. In summary, here we describe a facile approach to increasing the safety of batteries by minimizing the risk for electrochemical burn if the batteries are inadvertently ingested, without the need for modification of most battery-powered devices.**

coin cell battery ingestion | battery-induced injury | ingestion of foreign bodies | button battery safety | esophageal injury

**B**attery ingestion in the pediatric population has been documented for decades and results in an estimated 5,000 emergency room visits per year (1). Of particular concern are button batteries, which can lodge in the esophagus and lead to serious complications, including death. The U.S. Consumer Product Safety Commission has analyzed data from 1997 to 2010 and estimated that 40,400 children younger than 13 years received treatment in hospital emergency departments for battery-related injuries, with 14 battery-related deaths in children from 7 mo to 3 y in age (1). Recent data from the National Capital Poison Center note that 3,366 reported battery ingestions occurred in 2013, with 2,277 occurring in the <6 y age group, and with 8% of these leading to adverse events, including major clinical complications, including death (2, 3). To help protect children from battery accidents, the Consumer Product Safety Improvement Act of 2008 was passed, which mandates toy safety standards (known as F963-11) and requires batteries to be inaccessible in all toys intended for children younger than 3 years. Unfortunately, additional legislation to further regulate the safety associated with button cell batteries (the Button Cell Battery Safety Act of 2011) introduced on June 9, 2011, in a previous session of Congress, was not enacted. This new legislation would have required warning labels and more secure battery compartments on a wide range of products, including watches, cameras, calculators, laptops, and smart phones. Although progress has been made to regulate safety by restricting battery access, improving the safety of batteries

themselves has not been addressed. In fact, newer, higher-voltage batteries such as the 3V lithium-ion batteries, particularly in the  $\geq 20$ -mm format, which can also be modified using the described approach, are recognized as leading causes of complications if ingested (4).

Injuries and sequelae from inadvertent battery ingestion include vocal cord paralysis, esophageal strictures, esophageal perforation, tracheoesophageal fistula, and aortoesophageal fistula leading to death (1, 5–8). It has been recognized for more than 30 y that esophageal impaction is associated with the most severe morbidity (7). Battery-induced injuries are proposed to occur via three mechanisms: ischemic necrosis from direct pressure, leakage of caustic alkaline electrolytes, and the generation of an external electrolytic current generating hydroxide at the negative pole of the battery (1, 3, 8–10). It is this last mechanism that leads to significant tissue injury (3). Because the interval from ingestion to injury is only 2 h (11), current management guidelines recommend endoscopic evaluation for foreign body retrieval in all cases of battery ingestion (5, 12).

To mitigate injuries caused by battery ingestion, here we report the development of pressure-sensitive, waterproof quantum tunneling composite coated (QTCC) button batteries based on off-the-shelf components. A QTC was applied to the anode of conventional button batteries to impart pressure-sensitive conductive properties. QTCs consist of conductive metal microparticles suspended in an insulating polymer matrix. Nanoscale roughness on the microparticle surface enhances the electric field gradient, such that when the particles come into close proximity (less than 1–5 nm), electrons can tunnel through the

## Significance

**Accidental battery ingestion in children is a recognized source of significant morbidity and mortality. To mitigate the risks of accidental battery ingestion, legislation has been introduced to regulate the locking of battery compartments. Regulation of battery housings has translated into modest reductions in the number of battery ingestion cases reported. We report here the fabrication of waterproof, pressure-sensitive battery coatings that are nonconductive in the low-pressure gastrointestinal tract, yet conduct in higher-pressure standard battery housings. These safer batteries are expected to reduce complications from accidental battery ingestion.**

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Conflict of interest statement: A provisional patent application for the technologies described herein was filed by B.L., R.L., and J.M.K. on March 13, 2013.

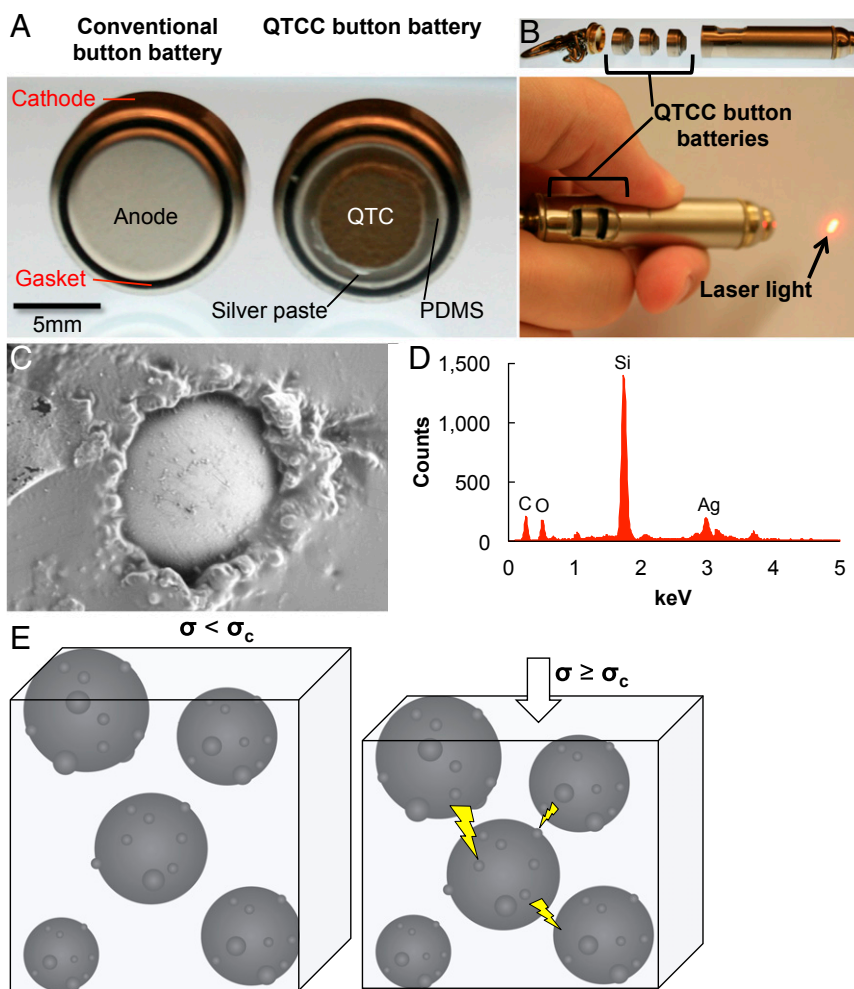
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insulator, separating them to conduct current (13, 14). Given that quantum tunneling does not require contact between the metal particles, the polymer matrix can remain continuous, and therefore waterproof (13, 14). Because of the low water permeability of silicone, the time to water ingress exceeds gastrointestinal transit time. A conductive paste affixes the QTC to the button battery anode, and an additional waterproof insulating polymer covers the remainder of the anode and gasket so that the button battery will not short circuit in conductive fluids below the compressive stress ( $\sigma_c$ ) level required for QTC conduction, avoiding the generation of external electrolytic currents if ingested. To evaluate the improved safety of QTCC batteries, we tested the batteries in a large-animal model simulating esophageal impaction. The pressure at which the QTCC batteries conduct is directly proportional to the coating thickness for a

given density of conductive microparticles. When the microparticles have higher average spacing at zero stress, greater axial compression is required to bring them into close enough proximity to achieve conduction. Because the QTCCs are affixed to the rigid battery housing, compression is restricted to the axial direction. Therefore, the required pressure for conduction is not diameter-dependent and can be applied to any diameter button battery without significant design modification. Moreover, given that conduction is directly proportional to coating thickness and particle density, significant tunability exists for triggering conduction. QTCCs impart weatherproofing of batteries, expanding the possible applications beyond accidental ingestion scenarios to include using batteries in high humidity or more corrosive environments that would otherwise affect the battery structure.



**Fig. 1.** Waterproof, pressure-sensitive, QTCC button batteries. (A) Photograph of conventional and QTCC button batteries. On the conventional button battery, the anode, cathode, and gasket separating them are labeled. To insulate the anode from short circuiting with the cathode in conductive aqueous media, a QTC is affixed to the anode with conductive silver paste. The remainder of the anode and gasket are covered in electrically insulating, transparent silicone (PDMS). In the absence of compressive force, the QTC is insulating and becomes conductive above a threshold force. QTCC button batteries with QTCs that exhibit threshold forces above the maximum digestive compressive force can reduce or even eliminate the chance that an ingested button battery would short circuit and cause tissue damage. (B) A standard minilaser pointer is shown operating normally when its conventional button batteries are replaced with QTCC button batteries. The barrel of the laser pointer was milled to create a viewing window, which is the only modification made to the battery housing. The photograph demonstrates that QTCC button batteries can function in standard commercially available housings. (C) Scanning electron micrograph showing a conductive metal microparticle embedded in flexible polymer. The small surface features help to focus the electric field aiding current to tunnel through the insulating polymer when an applied force compresses the QTC, bringing the conductive particles into close proximity. (D) Electron dispersive spectroscopy X-ray analysis detects the elemental components of silicone rubber (Si, C, and O), the insulating matrix, and silver (Ag), the primary elemental component of the conductive microparticles. (E) Schematic cartoon of a cross-section of QTC material in the insulating state ( $\sigma < \sigma_c$ ), when the suspended conductive microparticles are too distant to enable charge transfer (Left) and in the conductive state ( $\sigma \geq \sigma_c$ ), when the nano-rough conductive microparticles are sufficiently close to enable quantum tunneling of electrons (Right).

## Results

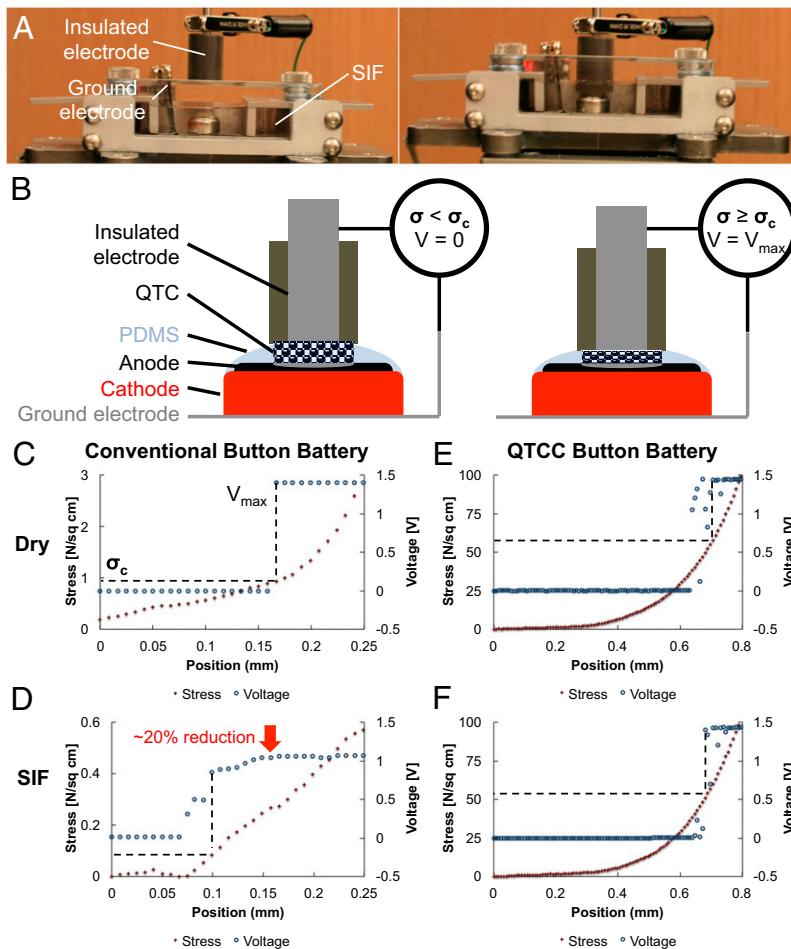
**QTCC Battery Design.** Conventional button batteries have circular anodes and cylindrical cathodes separated by insulating ring gaskets (Fig. 1A). To construct a QTCC button battery, a conductive silver paste affixes a QTC disk to the anode (Fig. 1A). Water-impermeable silicone rubber seals the area between the QTC edge and the cathode, bridging the remainder of the anode and gasket to thereby waterproof the battery. To demonstrate that QTCC button batteries function within standard button battery enclosures, three stacked QTCC button batteries were shown to power a commercially available laser pointer (Fig. 1B). Importantly, the materials used to construct QTCC button batteries are inexpensive and readily scalable for mass production.

A high-magnification scanning electron micrograph of the QTC shows a conductive metal microparticle embedded in compressible, insulating silicone polymer (Fig. 1C). Nanoscale features are present on the surface of the metal microparticles, which facilitate quantum tunneling between microparticles because electric field density enhancement increases nonlinearly with decreasing radius of curvature (11, 12). Electron dispersive X-ray spectroscopy peaks for silicon (Si), carbon (C), and oxygen

(O) can be attributed to the poly(dimethyl siloxane) (PDMS), and the silver (Ag) peak to the metal microparticles (Fig. 1D).

Fig. 1E shows a schematic depiction of a QTC with nano-rough silver microparticles suspended in PDMS. When the compressive stress exceeds  $\sigma_c$ , the metal microparticles are in close enough proximity that electrons can tunnel and conduct current, transforming the QTC from an insulator to a conductor. This mechanism allows QTCs to be insulating below compressive stresses of the gastrointestinal tract and conductive above compressive stresses of battery housings, at which QTCC batteries achieve maximum voltage ( $V_{max}$ ), while remaining impermeable to water.

**QTCC Battery Electromechanical Characterization.** To quantify the  $\sigma_c$  at which QTCC button batteries achieve their  $V_{max}$ , load and voltage were measured continuously between an insulated electrode and a ground electrode held in a water bath (Fig. 2A). Conventional and QTCC button batteries were tested in dry and simulated intestinal fluid (SIF) conditions. The insulated electrode is brought into contact with the battery by the mechanical testing apparatus, applying compressive stress while measuring voltage. Below  $\sigma_c$ , the QTC component of QTCC batteries remains an insulator. Above  $\sigma_c$ , the microparticles within the



**Fig. 2.** Mechanical and electrical properties comparison between conventional and QTCC button batteries. (A) Experimental setup used to test the threshold force beyond which QTCC button batteries will conduct in SIF. Compressive force and voltage are measured in real time. (B) Schematic diagram of a QTCC button battery compressed below and above the  $\sigma_c$  and when the circuit is completed, achieving  $V_{max}$ . (C) A dry conventional button battery conducts at  $V_{max}$  with low applied stress, as highlighted by the dashed lines, showing the compressive stress at which the battery first achieves conduction ( $\sigma_c$ ). (D) When immersed in SIF, a conventional button battery shows a  $\sim 20\%$  reduction in conduction voltage because of the short-circuit current leaked via the conductive fluid connecting the anode and cathode as an alternate conduction pathway. (E)  $V_{max}$  is reached at  $\sim 58 \text{ N/cm}^2$  by a QTCC button battery in dry conditions. The  $V_{max}$  is equal to that of a conventional button battery. (F) Immersed in SIF, QTCC button batteries require similar levels of compressive stress to achieve conduction. In addition, the  $V_{max}$  achieved is indistinguishably different from that in the dry state because of the waterproof design of QTCC button batteries.

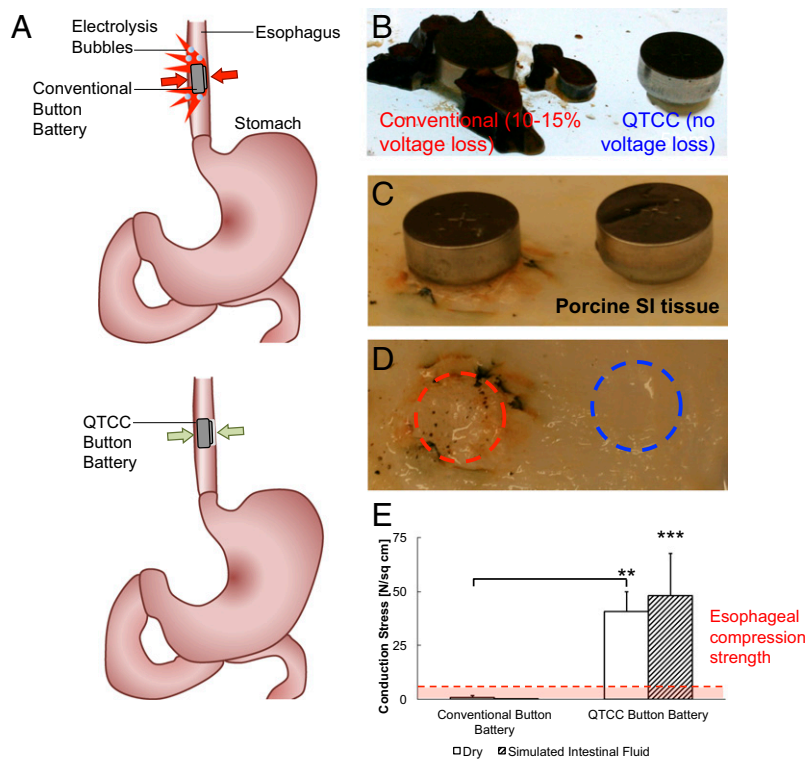


QTC conducts and the rigid polymer insulator surrounding the electrode form a seal with the compressive PDMS. Creating a waterproof seal with the simulated battery housing eliminates short circuit current paths from the anode to the cathode and enables the pressure-sensitive button battery to transmit its full potential difference ( $V_{max}$ ) to the voltage sensing circuit, even in the presence of conductive SIF (schematic shown in Fig. 2B).

Conduction stress was tuned in the QTC system to only enable conduction at pressures more than one order of magnitude above esophageal pressures encountered in certain spastic disorders; namely, nutcracker esophagus, in which high esophageal pressures are encountered ( $>180$  mm Hg,  $2.4$  N/cm<sup>2</sup>) (15). This high-pressure barrier for conduction was chosen for maximal safety, even in patients with this rare disorder. Fig 2 C–F shows simultaneous stress and voltage recordings from conventional and QTCC button batteries. Minimal applied stress is required to make contact with the anode and cathode of conventional button batteries, yielding conduction to achieve the  $V_{max}$  output (Fig. 2C). These measurements were performed independent of time. In SIF, conventional batteries leak current as a result of the short circuit current established by the conduction pathway from the anode through the ionic fluid to the cathode, producing an

immediate 20% reduction in measured voltage (Fig. 2D). Unlike conventional button batteries, QTCC button batteries retain their voltage and output current when submerged in SIF; furthermore, they require significantly greater compressive stress ( $>1,875$  mm Hg,  $>25$  N/cm<sup>2</sup>) than conventional button batteries before they conduct (Fig. 2E and F). Once the QTC critical stress is applied, the pressure-sensitive button battery conducts with the same voltage as a conventional button battery. This demonstrates that incorporation of QTCs does not compromise the conductive state of button batteries and, instead, expands their application range to include conductive fluid environments.

QTCC button batteries require approximately an order of magnitude greater compressive stress than measured in the esophagus to achieve conduction (Fig. 3E). Because conventional batteries conduct in simulated intestinal fluid, whereas pressure-sensitive QTCC button batteries require stress in excess of that experienced in the gastrointestinal tract of adult humans, even in rare spastic motility disorders (depicted in Fig. 3C), QTCC button batteries should drastically lessen or even eliminate the button battery short circuiting after ingestion. We initially evaluated this by in vitro exposure of porcine gastrointestinal tissue to conventional and QTCC button batteries (Fig. 3C and D and



**Fig. 3.** Comparison between QTCC and conventional batteries  $\sigma_c$  at which  $V_{max}$  is achieved and in vitro testing. (A) Schematic of ingested conventional button battery injuries in the esophagus. When conventional batteries contact or are pressed against gastrointestinal mucosal tissues, their short circuit current and electrolysis cause injury. QTCC button batteries do not short circuit either in contact with or as a result of pressure produced by gastrointestinal motility, increasing safety if ingested. (B) Photograph of a conventional (Left) and QTCC (Right) button battery after 48 h of immersion in SIF. The conventional battery has leaked a substantial portion of its contents because of short circuiting, whereas the QTCC button battery remains intact. (C) After 2 h in SIF, conventional button batteries short circuit, inducing significant damage on porcine small intestinal tissue, whereas QTCC button batteries cause no apparent gross tissue damage. A side-view photograph of porcine intestinal tissue after 2 h of immersion in SIF with a conventional (Left) and a QTCC (Right) button battery shows significant tissue damage only beneath the conventional battery. (D) Top-view photograph of porcine small intestinal tissue after batteries have been removed, showing the lack of damage beneath a QTCC button battery highlighted in blue and the significant tissue damage beneath a conventional button battery highlighted in red. **Movie S1** is a time-lapse video spanning the 2-h porcine intestinal exposure period. (E) QTCC button batteries require statistically significantly higher compressive stresses to induce current flow than conventional button batteries in dry and SIF conditions ( $**P \leq 0.01$  dry,  $***P \leq 0.001$  SIF). Esophageal crush strength was determined by manometry (15). The red dashed line depicts the highest pressures expected in the esophagus during swallowing for both humans and dogs, who are often injured by accidental battery ingestion, and pigs, which were used for large-animal safety testing. The average conduction stress for QTCC button batteries is an order of magnitude greater than esophageal manometry readings, which indicates that QTCC batteries, unlike conventional button batteries, should not short circuit after ingestion.  $n = 3$ ;  $**P \leq 0.01$ ;  $***P \leq 0.001$ .

Movie S1). Moreover, QTCC batteries maintain their integrity even when exposed to SIF, whereas conventional batteries conduct sufficient electrolytic current to degrade the conventional battery gaskets, leading to battery content release (Fig. 3B).

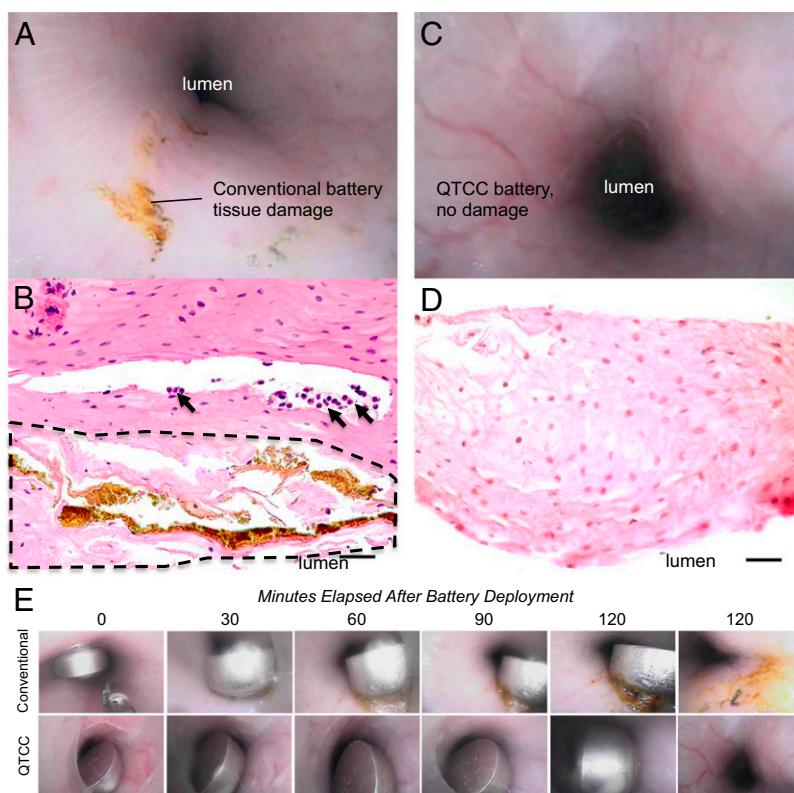
**Large-Animal Esophageal Safety Testing.** QTCC batteries were evaluated in an *in vivo* esophageal battery retention model in which batteries were repeatedly evaluated endoscopically through the use of an esophageal overtube (inner diameter, 16.7 mm), thereby ensuring the test batteries remained stationary, approximating esophageal battery retention. Conventional and QTCC batteries were deployed in the swine esophagus, with the anode positioned on the posterior aspect of the esophagus of an animal in the supine position. Conventional batteries were noted to leak battery content (Fig. 4A) over the course of 2 h during endoscopic evaluation. Microscopically, esophageal tissue exposed to conventional batteries for 2 h exhibited necrosis (as evidenced by desquamation and loss of nuclei), as well as a neutrophilic infiltrate (Fig. 4B). In contrast, swine esophagus continuously exposed to QTCC batteries appeared normal, both macroscopically and microscopically (Fig. 4C and D). In summary, QTC coatings protected the esophageal mucosa from any battery-associated damage in three separate QTCC battery experiments compared with three experiments with control (uncoated) batteries that demonstrated battery content leakage and mucosal damage. This

supports the potential for improved battery safety with the QTCC system.

## Discussion

Inadvertent battery ingestion represents a preventable medical emergency. Mitigation of the risks associated with this clinical state has, until now, focused on policy enactment, with associated “locking” of the battery chambers that house the button batteries. Since the introduction of the Consumer Product Safety Improvement Act of 2008, there has only been a modest decline in the number of reported battery ingestions, going from 3,461 in 2009 to 3,366 in 2013 (2). Here we report an approach that, in concert with ongoing policy and legislative agenda, has the potential to significantly reduce complications from the ingestion of button batteries.

We have taken an approach of maximizing the safety of the button battery, directly addressing the control of current transmission, through a simple and inexpensive coating approach that disallows current flow in the gastrointestinal environment. We have demonstrated that QTCCs have the capacity to insulate and prevent current transmission in both the dry state and the conductive environment of SIF. Furthermore, we have demonstrated that conventional batteries, once coated with QTC, retain the capacity to power a device and that through the differential pressure on the QTCC batteries, triggering of current transmission can be modulated.



**Fig. 4.** *In vivo* evaluation of conventional and QTCC button batteries in the swine esophagus. (A) Conventional and QTCC batteries were deployed in the swine esophagus, with the anode positioned on the posterior aspect of the esophagus of an animal in the supine position. Batteries were observed at regular intervals for 2 h to ensure they remained stationary, thereby simulating esophageal retention. Conventional batteries were noted to leak material (brown material) over the course of 2 h. (B) Histologic evaluation of biopsy samples taken from the site exposed to the battery at 2 h was notable for necrosis of the superficial squamous epithelium, as evidenced by desquamation and anucleated squamous cells. Furthermore, an intraepithelial bulla containing neutrophils is also present. Note also the brown pigment within the superficial layers of the esophageal squamous epithelium consistent with leaked battery material (---). Furthermore, a neutrophilic infiltrate was also notable (black arrows). (C and D) In contrast, the esophagus exposed to the QTCC button batteries appeared normal both macro- and microscopically, indicating no tissue damage. (Scale bars, 20  $\mu$ m.) (E) Endoscopic images acquired every 30 min of conventional and QTCC button batteries in the swine esophagus *in vivo*. The conventional battery demonstrates leaking of its contents starting at the 30-min point. The QTCC battery appears to remain intact throughout the test period.

In addition, we have demonstrated that insulated electrodes, such as those used in the electromechanical characterization of the critical stress of conduction ( $\sigma_c$ ), allow QTCC batteries to conduct at their full potential, even immersed in conductive fluid environments. Standard batteries under the same conditions will form electrolytic currents that have the potential to not only impart tissue damage but also cause the breakdown of the gasket separating the anode and cathode. Within hours after immersion, standard batteries begin to release their contents once the gaskets are compromised, whereas QTCC batteries show no signs of damage or current loss. Therefore, QTCC batteries also have the potential to function in aqueous and corrosive environments based solely on the QTC coating without requiring additional waterproof battery housings.

Further studies in animal models including evaluation of larger batteries and a broad range of batteries inclusive of the more recently developed 3V lithium batteries will be conducted to maximize translational potential. Furthermore, accidental impaction in orifices including the nose and ear will be evaluated in future studies. The platform we present has the capacity for extensive tunability to varying pressures, depending on the button battery-powered device requirements, by virtue of the QTC parameters. Implementation of safer button batteries should result in significant reductions in morbidity and mortality in the pediatric population in particular, as well as other vulnerable populations using button batteries, such as the elderly. Furthermore, by limiting moisture exposure, QTC coatings have the potential to lengthen the shelf life of batteries.

## Materials and Methods

**QTCC Button Battery Construction.** To construct QTCC button batteries, 1-mm-thick sheets of QTCs (Zoflex) were punched with 6-mm-diameter biopsies (Integra Miltex) to form disks. QTC discs were affixed to the anodes of conventional button batteries often used in hearing aids (Rayovac 675, 11.6 mm diameter, 5.4 mm height, 1.4V), using conductive silver paste (McMaster-Carr). Sylgard 184 (Dow Corning) silicone (PDMS) prepolymer and cross-linking agent mixture was applied in the area surrounding the QTC disk, ensuring that the edges of the QTC, exposed anode surface, and gasket were completely covered. Once the PDMS cured, the applied coating imparted waterproofing and pressure-sensitive conduction properties.

**QTCC Button Battery Functional Analysis.** To verify the functioning of QTCC button batteries in a device commonly powered by conventional button batteries, a miniature laser pointer (LaserPointerPro.com) was powered with three QTCC button batteries. The only alteration to the battery housing was a viewing window that was milled to enable visualization of the QTCC button batteries in action. The normal functioning of the laser pointer indicates that QTCC button batteries could readily be used in place of conventional button batteries.

**Morphological and Compositional Analysis.** The QTC surface was analyzed on a Zeiss Ultra55 field emission scanning electron microscope (Carl Zeiss AG) equipped with energy-dispersive spectroscopic elemental analysis.

**Electromechanical Testing.** To quantify the compressive stress at which QTCC batteries achieve  $V_{max}$  compared with conventional button batteries in SIF and dry conditions, batteries were placed between an insulated electrode and a ground electrode. A mechanical tester (ADMET) was used to simultaneously measure applied compressive force and voltage. Digital recordings of the electromechanical test were obtained and analyzed to calculate the contact area between the insulated conductive probe and the batteries.

**Simulated Intestinal Fluid Immersion Testing.** To determine how conventional and QTCC batteries would differ in a simulated intestinal environment, conventional and QTCC button batteries were immersed in phosphate buffer saline as a model for SIF (phosphate-buffered saline at pH 7.4; Life Technologies). Small intestinal tissue from Yorkshire swine was procured within 20 min of animal death and stored at 4 °C. All tissue was obtained from Research 87, Inc. Samples were placed anode-down on the mucosal side of porcine intestinal tissue for 48 h to simulate exposure for the full duration of gastrointestinal transit. After immersion, voltage was measured as described earlier to quantify loss. Samples were placed anode-down on the mucosal side of porcine intestinal tissue for 2 h while being digitally recorded or photographed.

**Statistics.** For single comparisons, an unpaired Student *t* test was used. For multiple comparisons, analysis of variance was performed with the Tukey's honestly significant difference test at significance levels of 95%. Error bars in bar graphs represent the SD.

**In Vivo Evaluation of QTCC Button Batteries.** In vivo porcine studies were performed in two female Yorkshire pigs weighing 65 kg. After induction of anesthesia with intramuscular injection of Telazol (tiletamine/zolazepam) 5 mg/kg, xylazine 2 mg/kg, and atropine 0.04 mg/kg, the pigs were intubated and maintained on isoflurane 1–3% (vol/vol). An esophageal overtube (Guardus overtube 50 cm; US Endoscopy) with an inner diameter of 16.7 mm was placed to enable facile and rapid esophageal access, as well deployment of the batteries. Control (uncoated) and QTCC batteries were deployed individually in varying segments of the esophagus. A total of three control (uncoated) and three QTCC batteries were evaluated. Individual batteries were evaluated one at a time by deployment in the esophagus and monitoring every 30 min endoscopically to ensure these remained stationary, thereby approximating esophageal battery impaction. To ensure the batteries remained stationary within the esophagus and to enable targeted biopsy sampling, batteries were placed immediately distal to the overtube, whereby the distal end of the overtube served as both a fiducial and guide for the location of the batteries. After 2 h, the batteries were removed and the site of battery placement biopsied for histological evaluation. All procedures were conducted in accordance with protocols approved by the Massachusetts Institute of Technology Committee on Animal Care.

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