

Evaluation and Stability of PEDOT Polymer Electrodes for Li–O₂ Batteries

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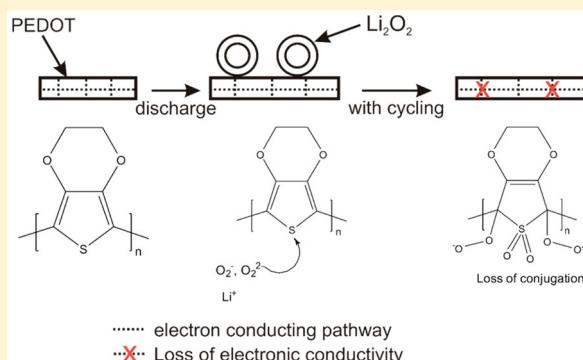
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Supporting Information

ABSTRACT: Lithium–air (O₂) batteries have shown great promise because of their high gravimetric energy density—an order of magnitude greater than Li-ion—but challenges such as electrolyte and electrode instability have led to poor capacity retention and low cycle life. Positive electrodes such as carbon and inorganic metal oxides have been heavily explored, but the degradation of carbon and the limited surface area of the metal oxides limit their practical use. In this work, we study the electron-conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) and show it can support oxygen reduction to form Li₂O₂ in a nonaqueous environment. We also propose a degradation mechanism and show that the formation of sulfone functionalities on the PEDOT surface and cleavage of the polymer repeat unit impairs electron conductivity and leads to poor cycling. Our findings are important in the search for new Li–O₂ electrodes, and the physical insights provided are significant and timely.



Lithium–air (O₂) batteries have shown promise as one of the energy-dense storage media of the future.^{1,2} With a theoretical energy density (3500 Wh kg⁻¹ Li₂O₂)¹ an order of magnitude greater than Li-ion, the quest for commercial Li–O₂ batteries has spurred great research interest. Despite their promise, Li–O₂ batteries have been plagued with numerous challenges such as electrode and electrolyte instability, slow oxygen reduction and evolution kinetics, poor capacity retention with cycling, and low cycle life.^{2–4} Commonly used electrodes such as carbon have been shown to be unstable in the presence of lithium peroxide (Li₂O₂) – the desired discharge product – and superoxide intermediates during cycling.^{5,6} Decomposition of carbon leads to insulating products such as lithium carbonate (Li₂CO₃) that are difficult to oxidize during charge and require high overpotentials.⁵ Other cathodes such as nanoporous gold,⁷ carbides,⁸ and inorganic metal oxides,⁹ among others, have been studied to replace carbon during Li–O₂ battery operation. Efficient cathodes for Li–O₂ need high surface area, good electronic conductivity, and low cost. Some electrode materials that may

present these desirable properties include carbides and inorganic metal oxides; however, the limited surface area of these systems, and the cost of precious relatively inert metals such as gold limit their wide applicability in Li–O₂ batteries. Electron-conducting polymers are attractive as they have the desired electrode properties and are very easily processed into different cathode structures. Despite the numerous cathode types examined for Li–O₂, only few reports examining electron-conducting polymers for Li–O₂ cathodes exist.

Conducting polymers such as poly(3,4-ethylenedioxythiophene) (PEDOT),¹⁰ poly(pyrrole),¹¹ and poly(aniline) have been widely explored as electrodes or electron-conducting binders for traditional Li-ion batteries. Typical binders such as poly(vinylidene fluoride) (PVDF) and polytetrafluoroethylene (PTFE) are not electronically conducting, and are used to bind composite electrodes. Poly(pyrrole) served as both binder and

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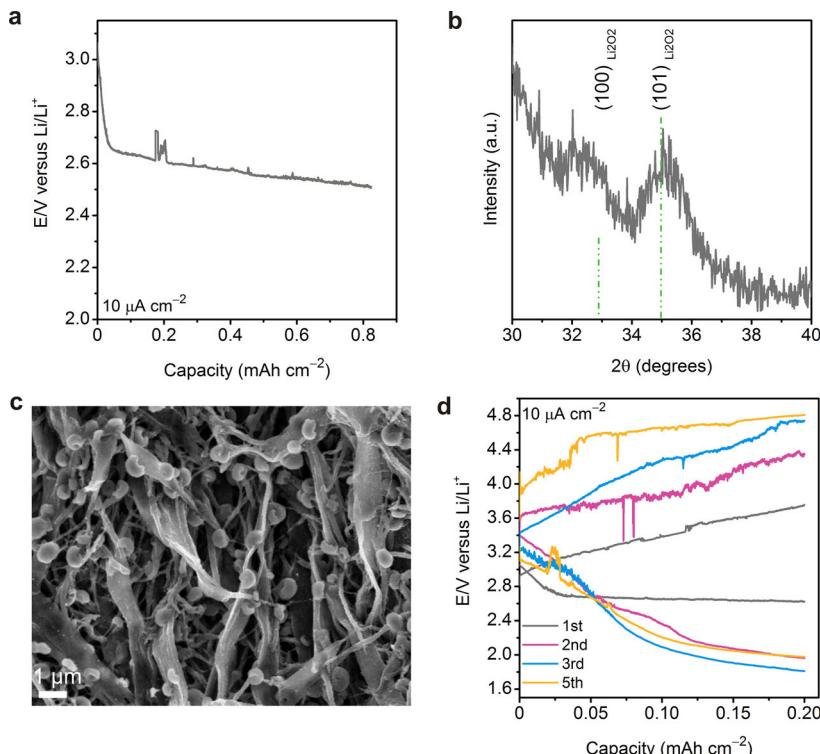


Figure 1. (a) Discharge curve of a Li–O₂ cell in O₂ at 10 $\mu\text{A cm}^{-2}$ using a free-standing PEDOT electrode; (b) X-ray diffraction (XRD) and (c) scanning electron microscopy (SEM) image after one discharge with a free-standing PEDOT electrode; (d) five cycles at 10 $\mu\text{A cm}^{-2}$ in O₂ using a free-standing PEDOT electrode. Figure 2a shows an SEM image of a pristine PEDOT electrode. Electrolyte: 0.1 M LiClO₄ in DME.

electron conductor with a LiMn₂O₄ cathode,¹¹ and PEDOT has been used to eliminate the conventional carbon electron conducting matrix.¹² Furthermore, coating active electrode materials such as lithium cobalt oxide (LiCoO₂) and iron oxyfluoride (FeOF) with PEDOT can improve kinetics and limit the degradation and side reactions between the active material and the electrolyte solvent.^{13,14} This strategy could be promising for Li–O₂ batteries where most organic insulating polymer binders such as PVDF have been shown to be unstable, as the ability of these conducting polymeric materials to transport electrons eliminates the need for further additives.^{3,15}

Cui et al.¹⁶ studied tubular poly(pyrrole) as an electrode for Li–O₂ batteries, and show formation of lithium peroxide and charge/discharge over multiple cycles. Yoon et al.¹⁷ recently reported the use of PEDOT:PSS (polystyrenesulfonate) to coat a graphene electrode, and claim that PEDOT:PSS can suppress undesirable side reactions in the Li–O₂ cell and improve cycling performance. Nasybulin et al.¹⁸ studied a Super P carbon/PEDOT composite as an electrode for Li–O₂ batteries, but the discharge performance and electrochemistry was dominated primarily by the carbon, and their use of a sulfone-containing salt like LiTFSI (lithium bis(trifluoromethane)sulfonimide) prevented a thorough understanding of PEDOT decomposition. The electron-conducting PEDOT was not evaluated as a stand-alone electrode despite its high electronic conductivity; serving primarily as a binder and contributing at most five percent of the obtained discharge capacity.¹⁸ In addition, these aforementioned studies did not explore the stability and mechanisms of degradation of the electron-conducting polymer upon cycling in Li–O₂ cells.

In this work, we examine the performance of a free-standing microstructured PEDOT electrode (with no carbon or binders

present) in a Li–O₂ battery and show that it can support lithium peroxide formation and Li–O₂ cycling. Our use of LiClO₄ as the electrolyte salt instead of LiTFSI enables clear understanding of the changes in the PEDOT structure. We show that the thiophene ring in PEDOT is susceptible to degradation that leads to sulfone formation, loss of conjugation in the polymer chain and diminished electronic conductivity that leads to poor cycling. Knowledge gained from this work provides greater understanding for using electron-conducting polymers as stand-alone Li–O₂ cathodes and for devising moieties that can avoid the observed degradation pathway of PEDOT. In addition, electron-conducting polymers could be used to coat inexpensive carbon particles to direct current and limit carbon reactivity and degradation in Li–O₂ cells.

The free-standing PEDOT films examined in this work were fabricated using an evaporative vapor-phase polymerization technique that generates the film directly from the substrate under conditions that yield fibrils of polymer film with nano- and microscale architectures.¹⁹ Other fabrication methods such as *in situ* deposition polymerization²⁰ or chemical vapor deposition (CVD)²¹ can also yield PEDOT films with select architectures and high electronic conductivity. Furthermore, the examined PEDOT films lack the PSS polymer often used to acidically dope the polymer and aid its solubility in aqueous solutions and some organic emulsions. The use of a PEDOT-only electrode avoids addition of functionalities (such as PSS) that may complicate the understanding of PEDOT activity and the monitoring of changes induced by Li–O₂ reactions. The doped PEDOT films generated in this work have high electronic conductivity (130 S cm⁻¹), and have been fully characterized by D'Arcy et al.¹⁹ The nanofibrillar architecture with high aspect ratio also makes it promising for Li–O₂ use

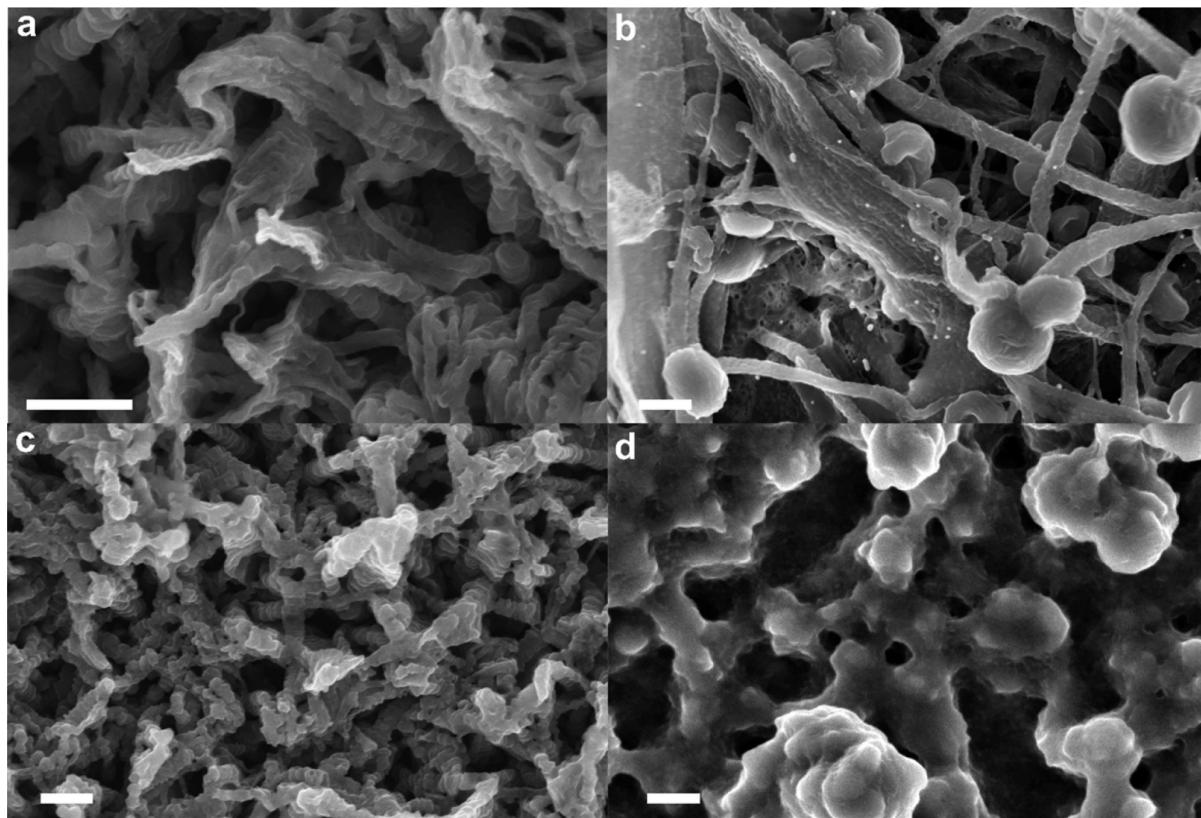


Figure 2. SEM images of pristine PEDOT electrode before discharge (a), after one discharge (b), one cycle (c), and five cycles (d). The free-standing PEDOT electrodes were discharged and charged at $10 \mu\text{A cm}^{-2}$ in O_2 in a 0.1 M LiClO_4 in DME electrolyte. Scale bar = 500 nm.

because it will provide abundant nucleation sites for Li_2O_2 growth.

The ability of PEDOT to support crystalline Li_2O_2 formation after discharge without the addition of catalyst or other electron conducting media such as carbon was explored. Using lithium metal as the anode and a 0.1 M LiClO_4 in DME electrolyte, PEDOT was able to support $\text{Li}-\text{O}_2$ discharge with a plateau at 2.6 V reminiscent of the voltage at which oxygen reduction occurs with other $\text{Li}-\text{O}_2$ battery electrodes (Figure 1a).²² Winter-Jensen et al.²³ have previously shown that the PEDOT surface is capable of supporting oxygen reduction, albeit in aqueous media. In conventional Li-ion batteries where PEDOT was evaluated as the electrode, low discharge capacities were observed because of poor intercalation of lithium ions into PEDOT. However, for $\text{Li}-\text{O}_2$ batteries, PEDOT does not need to host lithium intercalation, but provide an electronically conducting surface that can support the diffusion and adsorption of O_2 and its subsequent reduction. X-ray diffraction (XRD) of the discharged electrode (Figure 1b) shows that Li_2O_2 is the primary discharge product, as evident from the (100) and (101) crystalline peaks.^{22,24} Furthermore, using scanning electron microscopy (SEM), one can observe the toroidal morphology associated with Li_2O_2 formation along the walls of the PEDOT electrode (Figure 1c).^{22,24}

Next, the PEDOT $\text{Li}-\text{O}_2$ cell was cycled five times using a capacity-limited regime at 0.2 mAh cm^{-2} (Figure 1d). The first discharge is similar to that observed in Figure 1 with the 2.6 V discharge voltage. The first charge is completed below 4 V, which is promising because typical carbon-based electrodes have higher charging potentials above 4 V and low energy

efficiencies.^{5,6} Although the charging overpotential in the first cycle is low, subsequent cycling leads to higher discharge and charge overpotentials. By the fifth cycle, the discharge plateau is at 1.6 V with charge culminating at 4.8 V.

SEM (Figure 2) was used to track the changes in the PEDOT architecture that may explain the poor cycling in Figure 1d. Figure 2a,b shows a pristine and discharged electrode, respectively. As expected, toroids are abundant along the PEDOT network. After the first charge, Figure 2c shows disappearance of the Li_2O_2 toroids, revealing the original PEDOT structure. Therefore, PEDOT can support Li_2O_2 formation and oxidation in at least one cycle. By the fifth cycle, agglomerates are observed (Figure 2d) that may be due to accumulation of products from DME and PEDOT decomposition. DME is known to be unstable during $\text{Li}-\text{O}_2$ cycling,^{6,25,26} and prone to electrochemical oxidation above 4 V. The high charging voltages needed to complete charging on the PEDOT electrode may thus exacerbate the degradation of DME. Accumulation of insulating decomposition products, such as Li_2CO_3 and acetates,⁶ passivate the PEDOT surface, preventing oxygen reduction in subsequent cycles.

To understand the stability of PEDOT, X-ray photoelectron spectroscopy (XPS) was used. Although electrochemical reduction to superoxide and consequently peroxide can occur on the PEDOT surface, these species are highly nucleophilic and can chemically attack PEDOT. Figure 3 shows C (1s), S (2p), and O (1s) spectra of the pristine PEDOT electrode and the electrode after one discharge, one cycle (ending on charge), and five cycles (ending on charge). The S (2p) spectra in Figure 3 show significant changes in the chemical environment of the S atom in PEDOT. As cycle number increases, the

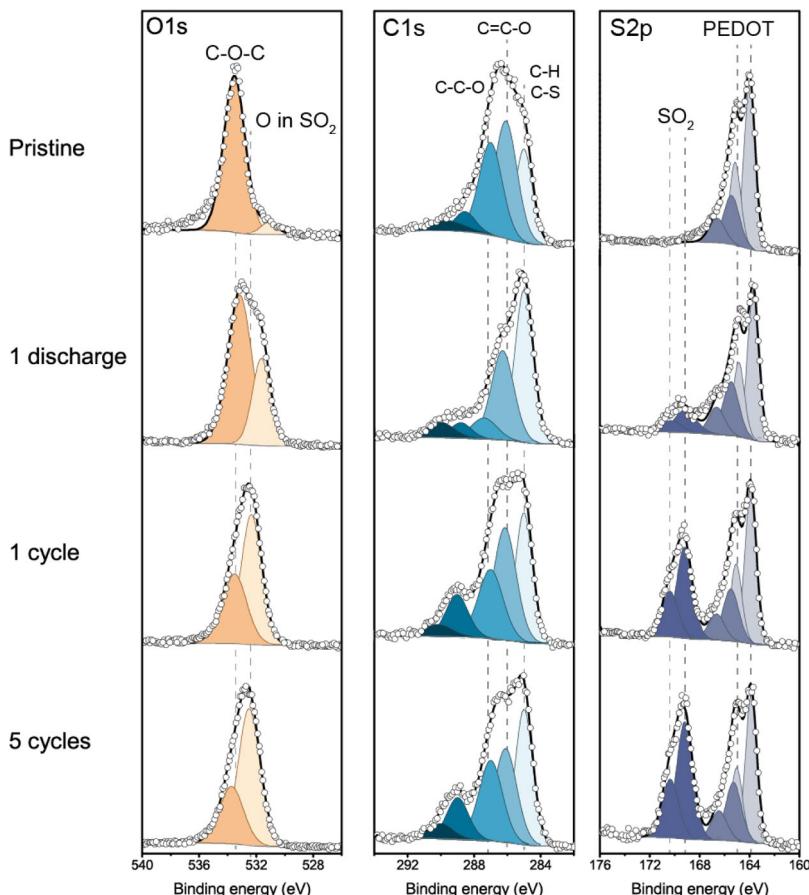


Figure 3. X-ray photoelectron spectroscopy (XPS) at the C (1s), O (1s), and S (2p) of a pristine PEDOT electrode, after one discharge, one cycle (ending on charge), and five cycles (ending on charge). The XPS spectra corresponds to the SEM images displayed in Figure 2. Details of the XPS deconvolution can be found in Supporting Information Table 1.

fraction of the higher binding energy peaks at ~ 169 (S 2p_{3/2}) and ~ 170 eV (S 2p_{1/2}) (relative to the original PEDOT peaks) increases. The shift to higher binding energy is due to sulfur atoms bound to a more electronegative atom like oxygen and those peaks have been attributed to sulfone.²⁷ Marcinak et al.²⁷ have shown that the PEDOT S atom can be attacked due to photooxidation and Verge et al.²⁸ have observed attack on the S atom in the presence of hydroxyl radicals.²⁸ Superoxide and peroxide anions are strong nucleophiles like hydroxyl, and may undergo similar reaction pathways with PEDOT (Supporting Information Figure 1).

The O (1s) spectra corroborate the observation in the S (2p) spectra. The fraction of the peak at 532 eV (compared to the total peak area) increases with cycling (Figure 4) and constitutes further evidence of the formation of a sulfone functionality. In addition, the extent of PEDOT oxidation is quantitatively analyzed using the O/S ratio by gauging the incorporation of extraneous oxygen onto the polymer surface or its bulk structure. After the first discharge, Li₂O₂ is observed as expected at around 531 eV in the O (1s) spectra²⁹ in Figure 3, and may account for the high O/S ratio observed in Supporting Information Table 2. However, with subsequent cycling that ends on charge, the O/S ratio is still higher than that observed in the pristine electrode and indicative of sulfone formation and oxygen-based DME decomposition species. The peak increase at 289 eV in the C (1s) spectra was postulated to be due to the formation of carbonyl/carboxyl groups on PEDOT or from DME oxidation or a shift due to the oxidized

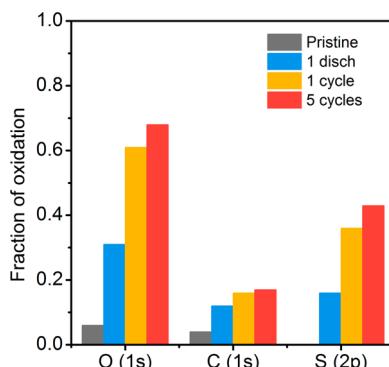


Figure 4. Fraction of oxidation products in the XPS O (1s), C (1s), and S (2p) spectra for the pristine PEDOT electrode, electrode after one discharge, one cycle (ending on charge), and five cycles (ending on charge). These fractions correspond to the XPS data in Figure 3. O (1s) fraction of oxidation = (532 eV peak area/total peak area); C (1s) fraction of oxidation = (289 and 290 eV peak area/total peak area); S (2p) fraction of oxidation = (169 and 170 eV peak area/total peak area). The S (2p) spectra for the pristine has no peaks at 169 and 170 eV and has a "0" fraction.

thiophene ring.²⁷ As Figure 4 shows, the fraction of oxidized products in the O (1s), C (1s), and S (2p) spectra increases with cycling.

In Supporting Information Figure 1, we propose a mechanism for PEDOT degradation where oxygen reduction products from discharge and charge attack the partially positive

S atom on the thiophene ring. A sulfoxide unit results and further addition to the S atom leads to formation of sulfone. Other sites on the PEDOT chemical structure can also be attacked as Verge et al.²⁸ show that OH radicals can oxidize the C–S–C bond. The formation of the sulfone functionality on the PEDOT ring is an irreversible chemical change and has been shown to lead to cleavage of the polymeric chain and a loss of conjugation.^{27,28} Conjugation across the polymer backbone is responsible for electron conduction; therefore, the loss of conjugation decreases electronic conductivity, and may explain the inability of PEDOT to sustain further oxygen reduction after the first cycle (Figure 1d).^{30,31}

In this work, we examined the performance of PEDOT as a stand-alone electrode in a Li–O₂ battery. We show that the conducting polymer PEDOT can initially support Li–O₂ discharge and charge with the formation and oxidation of Li₂O₂, respectively. However, after several discharges and charges, irreversible changes occur on PEDOT that lead to the oxidation of the thiophene ring and formation of sulfone, cleavage of segments of the polymer that leads to loss of conjugation and electronic conductivity; these changes result in poor cycling behavior. Therefore, the use of PEDOT is limited for binder or electrode use in Li–O₂ batteries. Knowledge gained from this work should galvanize the Li–O₂ community in developing new electronic conducting polymers that avoid the susceptibility of PEDOT S atom oxidation and loss of conjugation, and provide an alternative to the carbon and inorganic electrodes that have been heavily studied so far. These findings are important in the search for new Li–O₂ electrodes, of which electron-conducting polymers are an exciting prospect, and the physical insights related to PEDOT decomposition are significant and urgent.

■ EXPERIMENTAL METHODS

Synthesis of PEDOT Electrode. The free-standing PEDOT electrode was synthesized as previously reported in ref 19 using an evaporative vapor-phase polymerization procedure. In a chemical vapor deposition (CVD) chamber, a droplet of FeCl₃ aqueous oxidant solution is placed on a gold-coated substrate. An EDOT in chlorobenzene solution is also introduced into the chamber, and the temperature is ramped from 25 to 130 °C at 600 °C/h for polymerization to occur. The PEDOT is removed from the chamber, washed with water and methanol to remove excess oxidant, and stored in 6 M HCl. To prepare for Li–O₂ use, the electrodes were washed in copious amounts of Milli-Q water (18 mΩ cm) before washing with methanol. The electrodes were then vacuum-dried at 75 °C for at least two nights. The PEDOT electrode was soaked in excess 0.1 M LiClO₄ in DME electrolyte prior to cell fabrication.

Fabrication of Li–O₂ Cell. Li–O₂ cells were fabricated in an argon glovebox (MBRAUN, H₂O < 0.1 ppm, O₂ < 0.1 ppm). Using Li–O₂ cells fabricated in our laboratory,³² 15 mm thick lithium metal (Alfa Aesar, 99.9% metals basis) was used as the anode, a 0.1 M LiClO₄ in DME electrolyte (BASF), two 18 mm Celgard C480 separators, and the PEDOT electrode. A stainless steel mesh (12.7 mm diameter) was used as the current collector. After fabrication, the Li–O₂ cell was moved without air exposure to another argon glovebox (MBRAUN, H₂O < 0.1 ppm, O₂ < 1%) where it was pressurized with oxygen. The fabricated Li–O₂ cell was allowed to rest for 4 h before any electrochemical tests were performed. After the electrochemical tests, the Li–O₂ cell was opened in an argon

glovebox without air exposure, and the PEDOT electrodes were stored.

Scanning Electron Microscope (SEM) Characterization. Samples were imaged using a Zeiss Supra 55VP and a Zeiss Ultra 55 (Carl Zeiss AG, Germany). The working voltage was 5 kV. Samples were mounted and sealed in an argon glovebox in order to minimize the time (~<5 s) of exposure to ambient atmosphere during transfer into SEM.

X-ray Diffraction Characterization. Electrochemically tested cells were opened in an argon glovebox (MBRAUN, H₂O < 0.1 ppm, O₂ < 0.1 ppm) without air exposure. Samples were sealed in an airtight XRD sample holder (Anton Paar, Austria) to minimize air exposure before and during XRD measurement. A Rigaku Smartlab (Rigaku, Salem, NH) in the parallel beam configuration was used to collect the XRD spectra.

X-ray Photoelectron Spectroscopic (XPS) Characterization. To avoid any exposure to air, samples were transferred from the glovebox to the XPS chamber using a sample transfer vessel (ULVAC-PHI, INC.) Spectra were collected with a PHI 5000 VersaProbe II (ULVAC-PHI, INC.) using a monochromatized Al K α source, a pass energy of 23.5 eV and a charge neutralizer. All spectra were calibrated with the C 1s photoemission peak of adventitious carbon at 285 eV. Photoemission lines were fitted using combined Gaussian–Lorentzian functions after subtraction of a Shirley-type background.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.jpclett.6b01986](https://doi.org/10.1021/acs.jpclett.6b01986).

Additional characterization and PEDOT degradation mechanism is provided. ([PDF](#))

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Notes

The authors declare no competing financial interest.

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