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A Review on Application of Poly(3,4-ethylenedioxythiophene) (PEDOT) in Rechargeable Batteries

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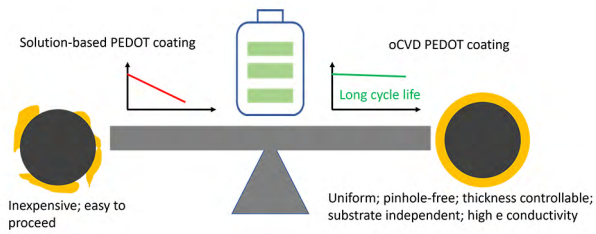

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Abstract Since the very first patent on poly(3,4-ethylenedioxythiophene) (PEDOT) that was filed in 1988, this polymer has been widely utilized and has achieved great success owing to its high electrical conductivity and excellent stability. The application of the conducting polymer, PEDOT, in renewable energy devices, especially rechargeable batteries, is attracting increasing attention due to its potential to solve the energy and climate crisis. In this review, we summarize the research over the past few decades directed toward the application of PEDOT in rechargeable batteries aimed at improving their electrochemical performance. We focus on PEDOT synthesized via oxidative chemical vapor deposition (oCVD), a relatively new process known for its ability to grow conducting polymer thin films with uniform, pinhole-free properties, and controllable thickness and conformality. For a comparison purpose, PEDOT synthesized via solution-based methods is also briefly summarized. Finally, future research directions for applying oCVD PEDOT in rechargeable batteries are discussed.

Introduction
PEDOT Synthesis Methods
Application of oCVD PEDOT in Rechargeable Batteries
Applications of Solution-Based PEDOT in Rechargeable Batteries
Conclusions and Outlook

Key words: polyethylene dioxythiophene (PEDOT), batteries, coating, oxidative chemical vapor deposition (oCVD)

Introduction

The importance of conducting polymers has been known for decades. The Nobel Prize in Chemistry in 2000 was awarded to Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa to acknowledge their contribution to the discovery and development of conducting polymers.[1] Polyethylene dioxythiophene (PEDOT), one of the most successful conducting polymers, has been attracting great attention in both the scientific and the industrial world since its first synthesis in 1988 by Jonas et al.[2] The invention of PEDOT solved a major challenge related to the commercialization of conducting polymers, which was the limited half-life conductivity originating from the poor air stability of doped states.[3] The stable conductivity and processability of PEDOT motivated its application as functional coatings, electrode materials, sensors, organic field-effect transistors, etc.[4]

Oxidative chemical polymerization and electrochemical polymerization of ethylene dioxythiophene (EDOT) are the two commonly applied methods to synthesize PEDOT. The reaction mixture is generally taken in an organic or aqueous medium where a surfactant is present to help improve the solubility of EDOT.[5] More recently in 2006, Professor Karen Gleason developed an oxidative chemical vapor deposition (oCVD) technique that can synthesize conformal coatings of conducting polymers, such as PEDOT, at low temperatures with controllable thicknesses ranging from a few nanometers to micrometers.[6] During the oCVD reaction, the EDOT monomer is vaporized and introduced into a vacuum chamber simultaneously with oxidant vapors. This leads to polymerization on the substrate surface. By controlling the substrate temperature, chamber pressure, type of oxidant, and deposition time, the thickness and physical properties of the polymer can be easily tuned.[7]

The first oCVD PEDOT reported by Lock et al. demonstrated an electrical conductivity of 105 S/cm.[8] Since then, oCVD PEDOT has been applied in various applications, including perovskite solar cells, supercapacitors, and sensors, and the electrical conductivity has been increased up to 7520 S/cm by increasing the crystallite size of PEDOT.[9] But oCVD PEDOT had not been applied to lithium batteries, one of the most important energy storage and conversion devices, until 2018 when Su et al. introduced it as a coating layer for lithium-ion battery (LIB) cathodes.[10] Since then, the application of oCVD PEDOT has been drawing increasing attention in the field of lithium batteries.[11]

Biosketches

Laisuo Su received his M.S. degree from Tsinghua University (China) in 2016 and his PhD degree from Carnegie Mellon University in 2021. Then, he joined Professor Arumugam Manthiram's group at the University of Texas at Austin as a postdoctoral fellow, and currently, he is a research associate. His research focuses on surface and interface engineering for developing next-generation batteries.

Shwetha S. Kumar received her bachelor's degree (B.Tech.) from National Institute of Technology, Tiruchirappalli, India in 2020 and is currently pursuing her PhD in the Department of Mechanical Engineering, Carnegie Mellon University (CMU). Her research focuses on the development of vapor deposited conducting polymer hybrid sensors for the detection of volatile organic compounds (VOCs) such as benzene and formaldehyde.

Arumugam Manthiram is the George T. and Gladys H. Abell Endowed Chair of Engineering at the University of Texas at Austin. His research interests are in the area of materials for rechargeable batteries and fuel cells, including new materials development and novel synthesis approaches. He has authored more than 900 journal articles with 95,000 citations and an h-index of 152.

B. Reeja-Jayan is an Associate Professor in Mechanical Engineering and Dean's Early Career Fellow at Carnegie Mellon University (CMU). Her lab synthesizes ceramic, polymer, and hybrid materials with low temperature and sustainable routes to enable decarbonization of process heating in the materials and chemical industry. These materials have been applied into lithium-ion battery devices and various types of sensors.

In this review, we specifically focus on the application of oCVD PEDOT in rechargeable batteries. The application of conventional solution-based PEDOT in batteries is also briefly introduced for comparison to highlight the advantages of oCVD PEDOT. By summarizing existing studies, we hope this review will stimulate the application of oCVD PEDOT in rechargeable batteries and the general adoption of the oCVD technique.

PEDOT Synthesis Methods

The properties of PEDOT depend on the counter-ions present and the packing as well as the length of the polymer chains. Hence, careful design of its fabrication process is critical for its use in various applications. PEDOT is generally synthesized by oxidative or electrochemical polymerization of its monomer, EDOT. The EDOT monomer can be oxidized to form cationic radicals. These radicals then undergo di-

merization, followed by deprotonation resulting in the formation of a neutral but active dimer. This active dimer can further get oxidized and continue the chain growth process. The neutral PEDOT chain is doped by the oxidant, with the anions from the oxidant acting as a counterion to maintain charge neutrality in the positively charged PEDOT. Thus, the role of the oxidant is two-fold: enable cation formation as well as dope the polymer chain.[12] There are two broad categories of synthesis methods: solution-based methods and vapor-based methods.

Solution-based methods have been widely adopted for synthesizing PEDOT, including wet chemical oxidative polymerization and electrochemical polymerization.[13] Figure 1a shows a schematic of electrochemical polymerization, where EDOT is oxidized by an applied potential and polymerization takes place at the working electrode.[13] The anions of the electrolyte are doped into PEDOT as counterions to stabilize the positive charge. The electrolyte can be changed to introduce different counter-ions and thereby adjust the conductivity of the resultant film. The doping and de-doping of PEDOT films can be controlled by changing the applied potential of the electro-polymerization reaction. Accordingly, the optoelectronic properties (e.g., ionic/electric conductivity, transparency, and Seebeck coefficient) can also be tuned.

Solution-based methods, though easy to replicate, have several limitations.[6] The substrate needs to be compatible with the oxidant and must not swell, degrade or absorb the oxidant. Wetting issues during the drying process could cause the polymer film to delaminate from the substrate. Also, electrochemical deposition methods require the use of a conducting substrate. This places a huge restriction on the type of substrates that can be employed. Moreover, solution-based methods suffer from surface tension defects. If high aspect-ratio structures are present on the surface of the substrate, the capillary effect will cause bridges to form between these narrow features, reducing the film conformality.[6]

Vapor phase polymerization is a partially solution-based process in which the oxidant is in the solution phase while the monomer is in the vapor phase. The oxidant is first applied onto the substrate in the form of a thin film generally by spin coating. It is then placed inside a chamber along with the liquid monomer and heated to a suitable temperature. The monomer vapors come in contact with the oxidant on the substrate surface and polymerization takes place. After removal from the chamber, the films can be washed with a suitable acid or alcohol solution to remove any unreacted oxidant as well as to promote dopant exchange. The addition of a base, such as a pyridine, in controlled amounts, can help suppress any acid-catalyzed polymerization, thus preventing unwanted side reactions from taking place and thereby improving the purity as well as conductivity of the film synthesized.[14]

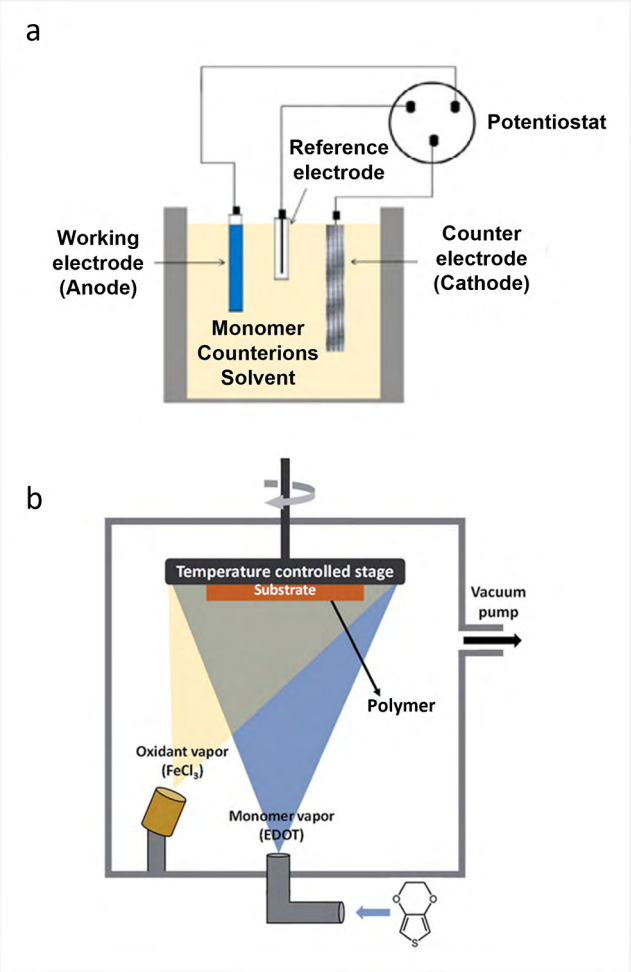

Figure 1 Schematic of (a) solution-based methods (electrochemical polymerization). Reprinted with permission from Ref. 13. Copyright 2021 Elsevier.[13] (b) Vapor-based methods (oxidative chemical vapor deposition) for the synthesis of PEDOT thin films. Reprinted from Ref. 7 published under a creative commons license (CC BY).[7]

Vapor-based methods tackle the abovementioned limitations by avoiding the liquid phase on the substrate. Figure 1b shows a schematic of the oCVD process for synthesizing PEDOT thin films.[7] In oCVD, reactants arrive at textured surfaces in the vapor phase, resulting in conformal and uniform PEDOT films that follow the contours of a complex substrate. The PEDOT film thickness and properties can be controlled by altering the chamber pressure and substrate temperature, monomer and oxidant temperature, monomer flow rate, and polymerization time. $FeCl_3$ is generally used as the oxidant to introduce dopants into the PEDOT film, which can also lead to different film properties, such as electrical and thermal conductivity. [6]

The advantages of oCVD are multi-fold. By eliminating the need to dissolve polymers to cast them into thin films, oCVD allows the synthesis of insoluble polymers and highly cross-

linked organic networks. It also enables the polymerization of monomer units that undergo unwanted side reactions in solution and the co-polymerization of pairs of monomers that lack a common solvent. Ultrathin pinhole-free films can be obtained, which is difficult to do with solution-based processing due to de-wetting and liquid thinning effects. High-quality films can be deposited as it is much easier to obtain high-purity vapors of low-molecular-weight monomers compared to their liquid-phase solutions.[6] The composition of the films can be easily controlled by temporally varying the flow rates of the monomers introduced. This has enabled the decoupling of the surface functionalities and properties from the bulk. These advantages enable high utilization of precursor materials and thus ensure the sustainability of the oCVD process. However, one limitation is the expensive cost of the oCVD devices and the complicated process steps to synthesize polymers. The other limitation is that the oxidants traditionally used in solution-based methods have low volatility and might decompose before sublimation. Thus, careful selection of oxidants must be made based on their volatility, thermal stability, and ability to drive the reaction forward.[6]

Application of oCVD PEDOT in Rechargeable Batteries

Rechargeable batteries, especially lithium batteries, have been attracting increasing attention in the past decade for their potential to solve energy and climate challenges. The incorporation of PEDOT has been shown to improve the performance of these batteries. It can be used as (1) a coating agent to protect the surface of battery active materials, (2) a binder to connect the active materials with super P carbon black, (3) a conducting additive to improve the electrical conductivity of the electrode, and (4) an electrode to store cations in rechargeable batteries, as shown in Figure 2a.

Figure 2b displays the number of research papers that have applied PEDOT in batteries in the past decade. Even though the number of papers is gradually increasing, the total number of research papers published in this field is still low. For example, the number of papers that apply PEDOT in batteries (73 papers) was less than 0.2% of the total number of papers in the battery field (39,542 papers) published in 2021. Moreover, most of these papers use solution-based methods for synthesizing PEDOT. Therefore, more attention needs to be paid to the application of oCVD PEDOT in batteries, where it has significantly improved the performance of lithium batteries, redox flow batteries (RFBs), and Al–air batteries (AABs).

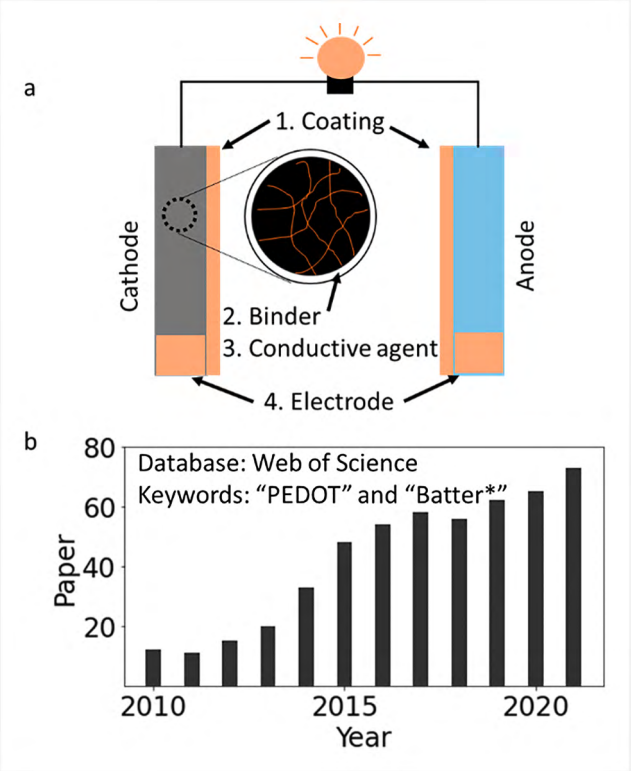

Figure 2 (a) Potential applications of PEDOT in batteries. (b) Statistical analysis of the papers on the topic of the application of PEDOT in batteries published from 2010 to 2021 based on the Web of Science Core Collection database. The keywords are listed in the figure.

Lithium-Ion Batteries

The application of oCVD PEDOT in LIBs was first demonstrated by Su et al. in 2018.[10] They pioneered the exploration of oCVD PEDOT to engineer the surface of battery cathodes, including $LiMn_2O_4$ and $LiCoO_2$.[10,15,16] The applicability on other cathodes, such as Ni-rich layered oxides, has also been demonstrated in recent works.[11] It is worth noting that the oCVD technique can engineer both individual cathode particles[11] and the entire cast-electrode with a conformal coating layer.[10,15,17]

Figure 3a shows a uniform PEDOT coating engineered on the surface of a $LiMn_2O_4$ particle via the oCVD technique.[10] The oCVD PEDOT coating improves the cycling stability of the $LiMn_2O_4$ electrode at a high temperature (50 °C) compared to a poly(divinylbenzene) coating (Figure 3b). The difference in effect on the cycling stability is attributed to the existence of chemical bonds between the polymer and the transition metal on the surface of the electrode. Su et al. further applied X-ray photoelectron spectroscopy and found that oCVD PEDOT can form chemical bonds with Mn. Such a chemical bond can inhibit the dissolution of Mn during cycling, thereby improving the cycling stability of the $LiMn_2O_4$

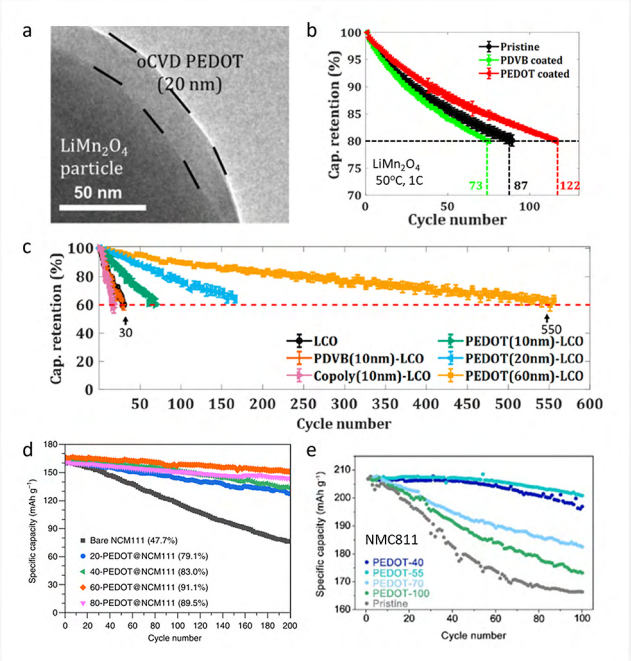

Figure 3 (a) TEM image of a 20-nm-thick oCVD PEDOT coating on a $LiMn_2O_4$ particle. Reprinted with permission from Ref. 10. Copyright 2018 American Chemical Society.[10] (b) The cycling performance of $LiMn_2O_4$ with different polymer coatings. Reprinted with permission from Ref. 10. Copyright 2018 American Chemical Society.[10] (c) The cycling performance of $LiCoO_2$ with different polymer coatings. Reprinted with permission from Ref. 15. Copyright 2021 American Chemical Society.[15] (d) The effect of PEDOT coatings with different thicknesses on $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC111). Reprinted with permission from Ref. 11. Copyright 2019 Springer Nature.[11] (e) The effect of PEDOT coatings with different thicknesses on $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811). Reprinted with permission from Ref. 17. Copyright 2022 Elsevier.[17]

electrode. Su et al. extended oCVD PEDOT coatings to the high-voltage applications of $LiCoO_2$, and they found that the cycling life of $LiCoO_2$ (at 4.5 V) could be increased by over 17 times with a 60 nm-thick oCVD PEDOT coating (Figure 3c).[3] Such a large improvement is attributed to the chemical bond formation between the S in PEDOT and the Co on the surface of the $LiCoO_2$ electrode. The oCVD PEDOT coating is more promising than inorganic coatings, such as TiO_2 and ZrO_2, to stabilize $LiCoO_2$ for its high-voltage applications.[18] Moreover, the rate performance of $LiMn_2O_4$ and $LiCoO_2$ is also improved by the oCVD PEDOT coating, which is critical to the fast charging of lithium batteries.

High-nickel layered oxides are attracting increasing attention due to their high practical specific capacity. Xu et al. demonstrated the applicability of oCVD PEDOT in various layered oxide cathodes, including $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC111), $LiNi_{0.85}Mn_{0.1}Co_{0.05}O_2$, and $Li_{1.2}Ni_{0.54}Mn_{0.13}Co_{0.13}O_2$, to improve their cycling stability.[11] They built a rotary oCVD system that can coat cathode particles with PEDOT. Figure 3d shows that the oCVD PEDOT coatings largely increase the capacity retention of NMC111 during cycling, regardless of the coating thickness. 60-nm-thick oCVD PEDOT shows the best protection of the cathode. They found that oCVD PEDOT coating can suppress the undesired transformation from the layered phase to the spinel/rock-salt phase and the associated oxygen loss, mitigate intergranular and intragranular mechanical cracking, and stabilize the cathode–electrolyte interface. These mechanisms explain the significantly improved cycling stability of the layered oxide cathodes after PEDOT coating.

Recently, Zhang et al. cast $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$(NMC811) on an Al substrate and coated oCVD PEDOT onto the cast electrode.[17] The PEDOT is chemisorbed on both the primary and secondary NMC811 particles with identified S–O bonds. Figure 3e shows that the oCVD PEDOT coatings largely increase the capacity retention of NMC811 during cycling, and the 55-nm-thick coating shows the best protection. Advanced characterizations show that oCVD PEDOT-coated NMC811 critically limits the formation of undesirable interphases on the cathode surface. The flexible nature of the polymer further provides enhanced resiliency to the cathode to accommodate volume changes during cycling. In addition, the adhesive ability of oCVD PEDOT reduces the number of polymer binders needed for casting the electrode, thus increasing the energy density of batteries.

Besides engineering the surface of battery electrodes, oCVD PEDOT has also been demonstrated to display strong electrochemical activity in the region of 2.0–4.2 V vs. Li/Li^+.[19] Moni et al. discovered that the small dopant anions (Cl^-) in oCVD PEDOT can easily move in and out of the polymer structure, allowing exchange with the Li^+ counter-ion in the solution. By comparison, the poly(styrenesulfonate) dopant in the PEDOT:PSS is a large macromolecule having much lower mobility. Figure 4a compares the electrochemical activities of oCVD PEDOT and PEDOT:PSS. The large currents of the two oCVD PEDOT films during the CV scanning indicate that they are electrochemically active from 2.0 to 4.2 V vs. Li/Li^+, while the negligible current of PEDOT:PSS

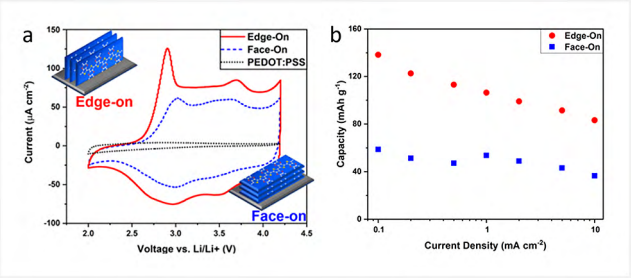

Figure 4 (a) CV measurement of oCVD PEDOT films and commercial PEDOT:PSS on stainless steel substrates with a scan rate of 10 mV·s^{-1}. (b) Specific capacities of oCVD PEDOT films with different current densities. Reprinted with permission from Ref. 19. Copyright 2018 American Chemical Society.[19]

suggests that it is electrochemically inactive. Two different orientations of oCVD PEDOT are realized by controlling the film growth temperature, with higher substrate temperatures promoting the growth of edge-on films. The edge-on oCVD PEDOT film shows the highest current during the CV measurement among the three tested films. Moreover, galvanostatic measurement further suggests that the edge-on film provides higher specific capacities at all the tested current densities compared to the face-on film (Figure 4b). The authors also paired the edge-on PEDOT with molybdenum disulfide to demonstrate the application of oCVD PEDOT films in high-rate electrochemical energy storage devices.

Redox Flow Battery

RFBs have emerged as promising energy storage devices because of their safety, long operational lifetimes, and the decoupling of energy and power scaling. Recently, Gharahcheshmeh et al. demonstrated the use of oCVD PEDOT in engineering the surface of carbon cloth electrodes for their applications in RFBs.[20] The oCVD PEDOT coating is proven to mitigate ohmic, kinetic, and mass transport losses of the electrode during application. Figure 5a shows that the conventional spun-cast PEDOT:PSS method cannot coat the carbon cloth electrode uniformly. The polymer-coated regions exhibit liquid bridging, non-conformality, and delamination. By comparison, the oCVD method helps form a conformal PEDOT coating on any porous and non-planar surfaces (Figure 5b), which is attributed to the absence of surface tension effects.

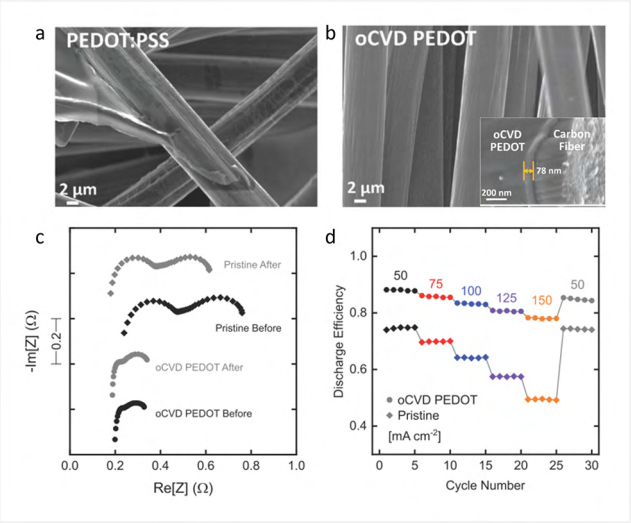

Figure 5 (a) SEM image of spun-cast PEDOT:PSS-coated carbon electrode. (b) SEM image of oCVD PEDOT-coated carbon electrode. The insert shows a cross-section SEM image of the coated carbon fiber. (c) Electrochemical impedance spectroscopy of the two carbon electrodes before and after the cycling test. (d) The evolution of discharge efficiency of the two electrodes at different current densities. Reprinted with permission from Ref. 20. Copyright 2020 John Wiley and Sons.[20]

The oCVD PEDOT coating on electrodes is electrochemically and mechanically resilient over long durations in RFBs. Figure 5c shows that the oCVD PEDOT-coated electrode shows similar electrochemical impedance before and after cycling, indicating that it is stable. The stability of the oCVD PEDOT coating is also supported by the cross-section scanning electron microscopy (SEM) images of the electrode after exposure to the electrolyte.[20] By comparison, the pristine electrode shows a large change in the impedance after cycling. Furthermore, the oCVD PEDOT-coated electrode shows over 80% discharge efficiency after several days of cycling, which is much higher than the pristine electrode (Figure 5d). Thus, the oCVD PEDOT coating protects the electrochemical and mechanical stability of the carbon electrode during long-term cycling.

Aluminum–Air Battery

Kuo et al. engineered oCVD PEDOT on the screen-printed MnO_2/carbon paper electrodes for an AAB.[21] They discovered that the composite cathode composed of oCVD PEDOT/α-MnO_2/carbon paper shows a higher discharge performance with improved conductivity compared to the cathode with the β-MnO_2 composite. The improved performance is attributed to the clear charge transfer between the oCVD PEDOT and α-MnO_2, which is supported by density functional theory calculations. Based on the study, they proposed that integrating the deposition of oCVD PEDOT and α-MnO_2/carbon paper as a composite electrode is suitable for use in AABs.

Applications of Solution-Based PEDOT in Rechargeable Batteries

While oCVD is an excellent technique for growing high-quality PEDOT thin films on battery electrodes, there is more ongoing research on a solution-based process to incorporate PEDOT into battery electrodes to improve their performance. Due to the surface tension of the liquid phase, the solution can hardly penetrate the porous structure of electrodes. Thus, the PEDOT film should be coated on the particles before casting the electrodes. As several review articles have already mentioned the application of solution-based PEDOT in energy storage devices,[4,22] we will briefly summarize the application of solution-based PEDOT in rechargeable batteries to highlight its shortcomings when compared to its vapor-based counterpart.

Like oCVD PEDOT, solution-based PEDOT has been extensively applied to engineer the surface of cathode materials to improve their performance in lithium batteries, including

$LiMn_2O_4$,[23] $LiCoO_2$,[24] $LiFePO_4$,[25] high-Ni layered oxides,[26] and Li-rich cathode materials.[27] Moreover, solution-based PEDOT has been demonstrated to be able to improve the cycling stability of Si anode[28] and sodium-ion cathodes.[29] Figure 6a shows PEDOT successfully coated on the surface of an NMC111 particle using a solution-based method.[26] However, the coating is not uniform. PEDOT coatings with different weight percentages help reduce the capacity fading of NMC111 during high voltage (4.5 V) cycling, and the 2 wt.% sample shows the most optimized electrochemical performance (Figure 6b). However, compared to the oCVD PEDOT coating shown in Figure 3, the solution-based PEDOT coating displays much less improvement in the electrochemical performance of cathode materials. The superior performance improvement of battery electrodes from the oCVD PEDOT coating can be further concluded from Table 1. The difference highlights the importance of applying the oCVD technique to modify the surface of battery electrodes with uniform and conformal polymer coatings in order to protect the electrodes against the electrolytes during cycling.

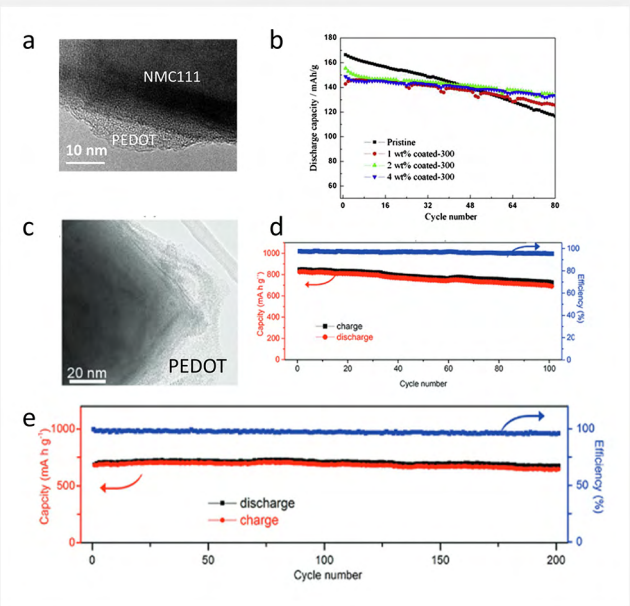

Figure 6 (a) TEM image of a PEDOT-coated NMC111 particle. Reprinted with permission from Ref. 26. Copyright 2013 Elsevier.[26] (b) Cycling performance of NMC111 cathode with different amounts of PEDOT coatings. Reprinted with permission from Ref. 26. Copyright 2013 Elsevier.[26] (c) TEM image of a PEDOT-coated Prussian blue nanocube ($S@Na_2Fe[Fe(CN)_6]$) for sulfur storage. Reprinted with permission from Ref. 33. Copyright 2017 John Wiley and Sons.[33] (d, e) Cycling performance of Li–S batteries with (d) original $S@Na_2Fe[Fe(CN)_6]$ cathode and (e) PEDOT-coated $S@Na_2Fe[Fe(CN)_6]$ composite cathode. Reprinted with permission from Ref. 33. Copyright 2017 John Wiley and Sons.[33]

Additionally, PEDOT : PSS has been explored as a binder to fabricate battery electrodes.[30] PEDOT : PSS not only enhances material conductivity but also forms a protective layer on the grains of active materials, suppressing electrolyte reduction and transition-metal dissolution. Shao et al. proposed a water-soluble composite binder consisting of carboxymethyl cellulose (CMC) and PEDOT : PSS.[31] This PEDOT : PSS/CMC composite has been used as an effective binder for various battery materials to improve their rate capability.[30]

Another important application of the PEDOT coating is in Li–S batteries.[32] The Li–S system offers a high theoretical capacity (1675 mA h·g^{-1}) and energy density (2567 Wh·kg^{-1}) given by the redox reaction between elemental sulfur and Li, which are much higher than those of transition-metal oxides. However, the polysulfide intermediates formed by the redox chemistry between S and Li can dissolve in the electrolyte, limiting the practical application of the Li–S system. Wang et al. applied PEDOT coating to reduce the diffusion of polysulfides entrapped in Prussian blue nanocubes.[33] Figure 6c shows that the PEDOT film is successfully coated on the surface of the Prussian blue nanocube $S@Na_2Fe[Fe(CN)_6]$ with a solution-based method. Figure 6d and 6e suggest that the PEDOT coating largely improves the cycling stability and the Coulombic efficiency (CE) of the

Table 1 A comparison of the two different PEDOT coating methods to engineering lithium-ion battery cathodes

Coating method	Cathode	Coating thickness	Test condition	Capacity retention before coating/ after coating @ cycle number	Ref.
oCVD PEDOT coating	$LiMn_2O_4$	19 nm	50 °C, 1C, 3.5 – 4.3 V	80 % @ 73 cycles/80 % @ 147 cycles	10
	$LiCoO_2$	60 nm	RT, C/2, 3.0 – 4.5 V	60 % @ 30 cycles/60 % @ 550 cycles	15
	$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$	60 nm	RT, C/10, 3.0 – 4.5 V	67.6 %/96.6 % @ 50 cycles	11
		60 nm	RT, 1C, 3.0 – 4.5 V	47.7 %/89.5 % @ 200 cycles	11
	$LiNi_{0.85}Mn_{0.05}Co_{0.1}O_2$	60 nm	RT, 1C, 2.7 – 4.3 V	54 %/91 % @ 100 cycles	11
	$Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$	60 nm	RT, C/10, 2.0 – 4.8 V	53 %/93 % @ 50 cycles	11
	$LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$	55 nm	RT, C/10, 2.8 – 4.3 V	80.5 %/97.1 % @ 100 cycles	17
Solution-based PEDOT coating	$LiMn_2O_4$	N/A	32 °C, 1C, 3.4 – 4.25 V	24 %/22 % @ 100 cycles	23
	$LiCoO_2$	N/A	RT, 50 mV/s, 2.9 – 4.2 V	50 %/100 % @ 50 cycles	24
	$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$	4 nm	RT, 1C, 2.8 – 4.5 V	70 %/89 % @ 80 cycles	26
	$Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$	5 – 20 nm	RT, 1C, 2.0 – 4.8 V	26.8 %/51.6 % @ 100 cycles	27

S@$Na_2Fe[Fe(CN)_6]$ cathode in Li–S batteries. They found that the PEDOT coating layer could accelerate electron transport and Li^+ ion diffusion, decrease the energy barrier for charge transfer, and eliminate the dissolution of sulfur and polysulfides in the electrolyte. These mechanisms explain the excellent capacity retention and high CE after even 200 cycles. It is worth noting that oCVD PEDOT has not been applied to Li–S batteries yet, which could be a promising research direction for the Li–S community.

Conclusions and Outlook

PEDOT is one of the most successful conducting polymers with an appreciable half-life of conductivity. The invention of oCVD technology enables the deposition of high-quality PEDOT films onto complex substrates with a controllable thickness. Despite the versatility of oCVD PEDOT, only a handful of research papers have investigated its application in rechargeable batteries. Compared to solution-based PEDOT, oCVD PEDOT can better improve the electrochemical performance of batteries owing to its high quality, substrate independence, coating conformality and uniformity, and high electrical conductivity.

(1) The oCVD technique can be used to coat cathode materials and electrodes for improving their rate performance and cycling stability. The applicability of oCVD PEDOT in $LiMn_2O_4$, $LiCoO_2$, and high-Ni layered oxides has been demonstrated and summarized in this review. Other conducting polymers, such as polythiophene, are also potential candidates. Additionally, the application of oCVD polymers on other promising cathodes should be considered, including $LiFePO_4$, Co-free $LiNiO_2$, disordered rock-salt, and even high voltage spinel ($LiNi_{0.5}Mn_{1.5}O_4$). The coating thickness, uniformity, and electrical conductivity need to be optimized to achieve the best performance of these cathodes.

(2) The oCVD technique can also be applied to engineer advanced anodes in LIBs. For example, it has been demonstrated that solution-based PEDOT can improve the performance of Si anodes by providing mechanical protection and electrical connection.[28] However, oCVD polymers have not been explored for their application in advanced anodes, such as Si and Si/graphite composite.

(3) The oCVD polymer coatings can protect the surface of alkali metals, such as Li and Na, for their application in alkali-metal batteries. As Li and Na metals are very active and thus can react with many solvents, such as water, the solvent-free oCVD technique is needed to engineer their surface to avoid damage during the surface engineering process. For instance, the development of lithium-metal batteries (LMBs) and anode-free LMBs are urgently needed to increase the energy density, which is limited by the uncontrollable Li dendrite growth.[34] The highly conductive oCVD PEDOT coating on the surface of Li metal can minimize heterogeneous Li nucleation and thus reduce the dendrite formation during cycling. Thus, the application of conductive oCVD polymers in alkali-metal batteries can largely promote further development in this field.

(4) Other battery systems, such as Li–S batteries, sodium-ion batteries, and sodium sulfur batteries, are also promising as energy storage and conversion devices. The poor stabilities of the cathode/electrolyte interface and anode/electrolyte interface limit their performance and practical applications. However, oCVD PEDOT coatings can overcome these limitations.

In summary, the versatile oCVD PEDOT has many advantages compared to solution-based PEDOT. The applicability of oCVD PEDOT in rechargeable batteries has recently been demonstrated as advantageous for improving their electrochemical performance. Nevertheless, the exploration of oCVD PEDOT and other oCVD polymers for their applications in rechargeable batteries is urgently needed to develop next-generation batteries.

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Conflict of Interest

The authors declare no conflict of interest.

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